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## Application of the Frenkel–Kontorova model to surface reconstructions

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**Abstract.** We apply the Frenkel–Kontorova model to the case of surfaces where the natural bond-length within the surface layer is different from the substrate bond-length. A reconstruction may occur in which the surface density of atoms is either less than or greater than the bulk density. The stability of the unreconstructed surface is controlled by the ratio of two parameters which have simple physical interpretations. We discuss the stability of real metallic surfaces in terms of the values of these parameters, with particular reference to the (111) surfaces of gold, platinum, iridium and aluminium.

### 1. Introduction

Surface reconstructions occur because the environment of atoms at a crystal surface is significantly different from that of bulk atoms and, as a result, the bonding of atoms at the surface is different from that in the bulk. A general feature of the bonding at metal surfaces is that the preferred inter-atomic bond-lengths within the surface plane are shorter than in the bulk. This effect is now thought to be quite large, the preferred surface bond-lengths being up to 10% shorter than in the bulk. In this paper we investigate whether this effect could be a driving force for surface reconstructions in which the density of surface atoms is larger than the bulk density.

There are several pieces of evidence that support the assertion that the natural bond-length at a metal surface is shorter than in the bulk. Experimental measurements have shown that the average lattice constant is reduced from its bulk value in small metal particles (Solliard and Flueli 1985, Salomons 1988). This indicates that surface bonds, which give a significant contribution to the average lattice constant of small particles, favour a shorter bond-length than those in the bulk. Calculations of the surface stress tensor for iridium, platinum, gold and aluminium surfaces have shown that these surfaces are under tensile stress (Needs 1987, Needs and Godfrey 1987, Needs and Mansfield 1989). The presence of a tensile surface stress indicates a tendency for the surface to contract within the surface plane. Furthermore, calculations of the equilibrium in-plane lattice constants of thin slabs of metal (Batra *et al* 1986, Dodson 1988) have shown that, in all the cases studied, there is a tendency for the surface region to prefer energetically a shorter lattice constant than in the bulk.

Because the bonds at a metal surface prefer to be shorter than those in the bulk one might expect the surface to reconstruct so as to reduce the average distance between the surface atoms. In fact this seldom occurs because there are two separate effects opposing

this possibility. Firstly, because the surface area of a crystal is essentially fixed by sample preparation, a reduction in the average distance between the surface atoms must be accompanied by an increase in the number of surface atoms. Atomic steps on the surface can act as sources of atoms, but removing an atom from a step and incorporating it within the surface layer will reduce the average coordination number of the atoms and presumably this costs energy. Secondly, if the distance between atoms in the surface layer is different from the bulk separation then the bonding with the substrate will be disrupted and this will also cost energy. We have argued (Needs and Mansfield 1989) that it is vital to include all of these effects in theories of surface reconstructions that involve changing the density of atoms within the surface layer.

In this paper we study a very simple model of a crystal surface and give the conditions for stability of the unreconstructed surface against reconstructions where the surface density of atoms is increased or decreased. We find that the stability criteria can be expressed in terms of the ratio of two parameters which have simple physical interpretations. Our model is the one-dimensional continuum form of the Frenkel–Kontorova ball and spring model (Frenkel and Kontorova 1938). This model has been studied extensively and exact solutions have been found (Frank and van der Merwe 1949, Bak and Pokrovsky 1981). Our treatment is similar to that of Frank and van der Merwe (1949) but the precise form of the stability criteria that we find is not the same as theirs because we are studying a somewhat different physical problem.

We will also discuss the stability of real metallic surfaces in terms of the values of the parameters of our model with particular reference to the close-packed (111) surfaces of gold, platinum, iridium and aluminium. Because of the uncertainty in the appropriate values of these parameters we will only be able to draw some rather general conclusions about the stability of real surfaces, but we hope to encourage others to calculate these parameters more precisely. The (111) surface of gold actually undergoes a reconstruction where the surface density of atoms is greater than the bulk density (Harten *et al* 1985) whereas the (111) surfaces of platinum, iridium and aluminium do not reconstruct. The idea of applying the Frenkel–Kontorova model to the gold (111) surface is not new; Harten *et al* (1985) noted that the form of the reconstruction bore a resemblance to the soliton solutions of the Frenkel–Kontorova model. In addition El-Batanouny *et al* (1987) fitted a form of the Frenkel–Kontorova model to the experimental data of Harten *et al* (1985), but in fact knowledge of the experimental structure alone does not give enough information to determine uniquely the values of the model parameters.

The Frenkel–Kontorova model is a very crude representation of a real surface. The model is one-dimensional and treats the surface region as a single layer. It includes interactions between surface atoms via springs between nearest neighbour atoms and includes the interactions with the substrate through a sine wave external potential. Furthermore we do not allow for the effects of atomic vibrations, so that our results are strictly applicable only at zero temperature. Whilst this model is not an accurate description of a real surface it does include, in a simple manner, each of the important effects that we believe must be present in a theory of surface reconstructions where the density of surface atoms is altered. In a previous paper (Needs and Mansfield 1989) we discussed the necessary ingredients of such a theory and concluded that three main effects were important:

- (i) the difference in natural bond-length between the surface layer and the substrate,
- (ii) the energy cost or gain of adding atoms to, or subtracting atoms from, the surface layer,
- (iii) the interaction between the surface and substrate atoms which accounts for the possible disruption of surface–substrate bonding caused by surface reconstruction.

The tendency to increase or decrease the density of surface atoms is a result of the competition (or collaboration) between effects (i) and (ii) in the list given above. Whether such a reconstruction actually occurs or not will also depend on effect (iii), which will tend to stabilise the unreconstructed surface.

## 2. A simple model with a smooth substrate

We begin by discussing a very simple model of a surface as a one-dimensional line of atoms connected by springs between nearest neighbours. We imagine that the line of atoms sits on top of a smooth substrate. The model thus includes the first two effects mentioned in section 1, but not the third, and is the Frenkel–Kontorova model in the special case of zero substrate potential (see section 3). The purpose of studying this model is to clarify the role of the energy cost of changing the density of atoms at the surface and to write this energy cost in terms of quantities that can be measured or calculated. We will derive a simple result for the energy change,  $\Delta E$ , associated with adding an atom to the surface. This energy change will play a central role in determining the stability of the surface.  $\Delta E$  can be split up into three contributions, the energy cost to remove an atom from a kink site at a step on the surface (which is equal to the bulk cohesive energy per atom), the energy gained by forming new surface bonds (which may be strained) and the change in energy that arises because all of the atoms must squash up a bit to make room for the extra atom. We will find that  $\Delta E$  is related to the strain derivative of the surface energy which is a quantity which can readily be calculated.

We model the surface as a line of equally spaced atoms with separation  $x$  lying on top of a smooth substrate. The surface has length  $L$  and contains  $N$  atoms, so  $Nx = L$ . We write the energy required to create the surface by cleaving the crystal as

$$L\gamma = N[\Gamma + \frac{1}{2}\mu(x - b)^2] \quad (1)$$

where  $\gamma$  is the surface energy per unit length,  $\mu$  is the spring constant and  $b$  is the natural length of the surface bonds. Equation (1) can be viewed as an expansion of the surface energy per atom,  $L\gamma/N$ , about the minimum value at  $x = b$  where the bonds are unstrained. The quantity  $\Gamma$  contains two terms, each contributing for every atom present in the surface layer. The first term is the negative of the chemical potential of the particle reservoir. The particle reservoir consists of the kink sites at atomic steps on the surface and the energy to remove an atom from such a kink site is the bulk cohesive energy per atom. The second term in  $\Gamma$  accounts for the new bonds that are formed as the extra atom is introduced into the surface. Because the coordination number of bulk atoms is larger than that of surface atoms we would normally expect the bulk cohesive energy per atom to be larger than the energy gained by forming new bonds at the surface and so  $\Gamma$  will, in general, be positive. Because we expect  $\Gamma$  to be positive we will refer to it as the energy cost per atom.

In this model the number of atoms within the surface layer,  $N$ , is allowed to vary so as to minimise the energy. Atoms will be added to, or subtracted from, the surface layer until equilibrium is reached, which corresponds to minimising the surface energy per unit length,  $\gamma$ . Because we have a smooth substrate this model can be solved trivially. In equilibrium all the atoms must be separated equally and hence the condition that the surface energy per unit length be minimised implies that  $d\gamma/dx = 0$ . This leads to the following solution for the equilibrium inter-atomic separation  $x_0$

$$x_0 = \left( b^2 + \frac{2\Gamma}{\mu} \right)^{1/2} \quad (2)$$

We will find it convenient to introduce the notion of surface stress (Shuttleworth

1950, Herring 1951),  $g$ , which, for our one-dimensional model, is the strain derivative per unit length of the energy required to form the surface *with the number of atoms in the surface layer fixed*. This is given by

$$g = (x/L) d(L\gamma)/dx = \gamma + x d\gamma/dx = \mu(x - b) \quad (3)$$

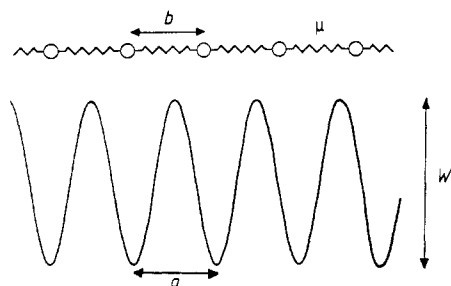
which is just the tension in the springs. Note that because we consider the infinitesimal strain to be applied rapidly compared with the time for atoms to migrate from step sites on the surface it is appropriate to consider the derivative with a fixed number of surface atoms.

The energy change,  $\Delta E$ , on addition of an extra atom to the surface layer when the surface inter-atomic separation is  $x$  (correct to order  $1/N$ ) can be obtained by differentiating equation (1) with respect to the number of surface atoms,  $N$ . This leads to

$$\Delta E = x\gamma - xg = -x(d\gamma/d\varepsilon) \quad (4)$$

where  $d\gamma/d\varepsilon$  is the strain derivative of the surface energy. When equilibrium is established  $\Delta E$  will be zero so that  $g = \gamma$  and  $d\gamma/d\varepsilon = 0$ , but we can argue that, for the unreconstructed surface,  $x(d\gamma/d\varepsilon)$  is a measure of the tendency to add atoms to, or subtract atoms from, the surface layer. If  $x(d\gamma/d\varepsilon)$  is positive then the addition of extra atoms to the surface layer will be energetically favourable, if on the other hand  $x(d\gamma/d\varepsilon)$  is negative it will be energetically favourable to remove atoms from the surface layer. Note that this is not necessarily implied by the presence of a tensile (positive) surface stress. A tensile surface stress indicates that the preferred surface bond-length is less than the substrate bond-length, but because there is an energy cost,  $\Gamma$ , associated with changing the number of atoms within the surface layer this does not imply that it is necessarily energetically favourable to increase the density of surface atoms. We should also point out that, for our model with a smooth substrate, the unreconstructed surface is always unstable to either adding atoms to or subtracting atoms from the surface layer. To obtain a region of stability for the unreconstructed surface we must consider a more realistic surface–substrate interaction.

So far we have considered the case of a smooth substrate. The inclusion of a non-zero surface–substrate potential will change the nature of the equilibrium solution of our model and it will no longer be true that, in equilibrium,  $g = \gamma$ . We can imagine that in general the effect of the surface–substrate interaction will be to give an additional energy cost for changing the density of surface atoms. This effect may be included by adding, for instance, a sine wave potential to the surface energy expression of equation (1) with minima at the substrate lattice positions (which for convenience we can choose to be at zero energy). When an interaction of this form is included we arrive at the Frenkel–Kontorova model (Frenkel and Kontorova 1938) which will be studied in the next section of this paper. We note that the inclusion of a substrate potential of this form does not change the surface energy of the unreconstructed surface because each atom lies at a zero of the substrate potential. To define a surface stress we must know how the substrate potential changes when a strain is applied to the sample. If we assume that the potential deforms with the applied strain so that the minima do not shift in energy then the substrate potential does not alter the surface stress of the unreconstructed surface. In fact the level of the substrate potential may shift with strain but inclusion of this effect would introduce another parameter into our model, and for the sake of simplicity we shall ignore this possibility. Hence we argue that, for a real surface with surface–substrate interactions, the magnitude of  $x(d\gamma/d\varepsilon)$  still measures the tendency of the surface to change its atomic density. This tendency will be opposed by the increase in energy due to the presence of the surface–substrate interaction which is composed of two parts: the



**Figure 1.** The one-dimensional Frenkel–Kontorova model. Each atom is connected to its two neighbours by springs of modulus  $\mu$  and natural length  $b$ . The atoms sit in an external sine wave potential of periodicity  $a$  and peak-to-peak amplitude  $W$ .

first is the direct interaction of the atoms with the substrate potential and the second is the extra strain energy in the surface bonds due to the fact that, in the equilibrium solution, the atoms will not be equally spaced. For the materials we have studied (aluminium, iridium, platinum and gold)  $d\gamma/d\varepsilon$  is calculated to be positive (Needs 1987, Needs and Mansfield 1989), indicating that reconstructions which involve increasing the density of surface atoms are possible but that reconstructions which lower the surface density are highly unlikely.

### 3. The Frenkel–Kontorova model

In this section we describe the Frenkel–Kontorova model which was briefly introduced in the previous section and is illustrated in figure 1. This model has the great advantage of being amenable to largely analytic solution though it contains the essential physics of the competing processes that we mentioned in the introduction to this paper. The Frenkel–Kontorova model has mainly been used to study the adsorption of atoms on surfaces and the stability of overlayers (Frank and van der Merwe 1949, Jesser and van der Merwe 1989) but clearly it can also be used to model the surface of a clean crystal where the natural bond-length within the surface layer is different from that of the substrate. We write the total energy,  $U$ , for  $N$  atoms as

$$U = \sum_{n=1}^N \left[ \frac{1}{2}\mu(x_{n+1} - x_n - b)^2 + \frac{1}{2}W \left( 1 - \cos \frac{2\pi}{a} x_n \right) + \Gamma \right] \quad (5)$$

where  $x_n$  is the  $x$  coordinate of the  $n$ th atom in the chain,  $\mu$  is the force constant of the springs,  $b$  their natural length and  $\Gamma$  is the energy cost associated with each surface atom which was discussed in section 2 of this paper. The substrate potential is a sine wave of amplitude  $W$  and periodicity  $a$ . Non-trivial solutions of this model arise because of the presence of competing periodicities; left to itself the surface would prefer a nearest-neighbour spacing of  $b$ , whereas the substrate is trying to force the atoms into bulk lattice positions whose spacing is  $a$ .

It is convenient to work in terms of the dimensionless coordinate  $u_n = (x_n - na)/a$ .  $u_n$  is a measure of the distance of the  $n$ th atom from the  $n$ th trough of the substrate potential; if  $u_n$  is integral then the  $n$ th atom sits in a potential minimum, if it is half-integral the  $n$ th atom sits on a potential maximum. Writing equation (5) in terms of  $u_n$  leads to

$$U = \sum_{n=1}^N \left[ \frac{1}{2}\mu a^2 \left( u_{n+1} - u_n - \frac{b-a}{a} \right)^2 + \frac{1}{2}W(1 - \cos 2\pi u_n) + \Gamma \right]. \quad (6)$$

The condition for a solution with no forces on the atoms is that  $\partial U/\partial u_i = 0$  for all  $i$ . This implies that

$$u_{i+1} - 2u_i + u_{i-1} = (W\pi/\mu a^2) \sin 2\pi u_i. \quad (7)$$

We now take a continuum limit in which the discrete label  $i$  is replaced by a corresponding continuous argument  $i$ . We expand the left-hand side of equation (7) as a function of  $i$  and retain only the lowest-order term. Equation (7) then becomes, having replaced  $i$  by  $n$ ,

$$d^2 u/dn^2 = (W\pi/\mu a^2) \sin 2\pi u. \quad (8)$$

The solutions of equation (8) give the equilibrium configurations of the chain within the continuum approximation. The summation over atoms in equation (6) becomes an integration over  $n$  and the energy of  $N$  atoms is

$$U = \int_0^N \left[ \frac{1}{2} \mu a^2 \left( \frac{\partial u}{\partial n} - \frac{b-a}{a} \right)^2 + \frac{1}{2} W (1 - \cos 2\pi u) + \Gamma \right] dn. \quad (9)$$

For our purposes we require the solution of equation (8) with the minimum *energy per unit length* of the surface, which corresponds to minimising the surface energy density. This is a slightly different condition from the one that is normally imposed which is to minimise the energy for  $N$  surface atoms.

#### 4. Solution of the Frenkel–Kontorova model

In this section we determine the criteria for stability of the unreconstructed solution of equation (8) where each of the atoms lies at the bottom of one of the potential wells. Note that  $\Gamma$  does not influence the form of the equilibrium equation, it merely shifts the relative energies of its solutions. Equation (8) may be integrated twice with respect to  $n$  to give the solutions with no forces on the atoms as was done by Frank and van der Merwe (1949). There are two branches of solutions: one in which the chain of atoms expands with respect to the substrate (i.e. the mean separation is greater than  $a$ ) and a second in which the chain contracts (and the mean separation is less than  $a$ ). The solutions describe a periodically repeated surface structure in which the unit cell contains either one more or one less atom than there are minima of the substrate potential in the same distance. The additional (or missing in the case of expansive solutions) atom results in a dislocation, or region of misfit, known as a soliton. The soliton density (and size of the periodic unit cell) is variable and depends upon one constant of integration.

We now derive the reconstruction criteria by considering the energy cost required to create a single compressive (or expansive) soliton in an unreconstructed chain. On performing the integration of equation (9) we obtain the energy,  $U$ , for a surface unit cell containing  $N$  atoms which we write as

$$U = U_1 + U_2 + U_3 + \Gamma N \quad (10)$$

where we have partitioned  $U$  so that we may physically interpret the origin of each term. The strain energy has been split into two parts  $U_1$  and  $U_2$ .  $U_1$  is the elastic energy the chain would have if the unit cell contained the same number of atoms but they were all equally spaced. This we call the homogeneous strain energy.  $U_2$  is the additional elastic energy the chain has due to the fact that the atoms in the unit cell are not all equally spaced; some are closer to each other than the average and some further apart. This we call the inhomogeneous strain energy.  $U_3$  is the potential energy of interaction of the surface chain with the underlying substrate. Finally,  $\Gamma N$  is the energy cost for the  $N$  atoms which was discussed in section 2. The three quantities  $U_1$ ,  $U_2$  and  $U_3$  are all positive.

For the unreconstructed chain, which is the solution to equation (8) with  $u(n) = 0$ , the energy of  $N$  atoms is given by equation (9) as

$$U = \frac{1}{2} \mu (a - b)^2 N + \Gamma N \quad (11)$$

the only contributions being the homogeneous strain term ( $U_1$ ) for atoms separated by

a distance  $a$  and the  $\Gamma$  term. The inhomogeneous strain energy ( $U_2$ ) is zero because all the atoms are equally spaced and the substrate interaction term ( $U_3$ ) is zero because all the atoms lie at zeros of the substrate potential. We now consider the energy of the solution of equation (8) which contains a single compressive (or expansive) soliton. In this case we can evaluate the integral in equation (9) to obtain the energy terms of equation (10), giving

$$U_1 + \Gamma(N \pm 1) = \frac{1}{2}\mu(a - b)^2(N \pm 1) \pm \mu a(b - a) + \Gamma(N \pm 1) \quad (12)$$

and

$$U_2 = U_3 = (1/\pi) \sqrt{2\mu a^2 W}. \quad (13)$$

In equation (12) the term  $\pm \mu a(b - a)$  is the correction to the homogeneous strain energy due to the single atom having been added to (or subtracted from) the infinite chain which results from the fact that the separation of the atoms will no longer be precisely equal to  $a$ . The positive signs in equation (12) correspond to the case where the atom is added to the chain and the negative to where it is removed. We note that equation (12) gives the energy the surface would have on addition (or subtraction) of a single atom in the absence of the sine wave substrate interaction. Equation (13) gives the additional energy cost  $U_2 + U_3$  due to the presence of the substrate potential. This latter term may be considered as the energy required to create a single isolated soliton and is the same whether the soliton is compressive or expansive.

We now evaluate the change in energy when one atom is added to the unreconstructed chain to form a single compressive soliton. The energy to add an atom to the chain such that the separation of the atoms remains uniform is obtained from equations (11) and (12) as

$$U_1 + \Gamma(N + 1) - U = \Gamma + \frac{1}{2}\mu(a - b)^2 - \mu a(a - b) = W\beta \quad (14)$$

which serves to define the dimensionless parameter  $\beta$ . Equation (14) is precisely the term  $\Delta E$  of equation (4) in the case where the separation of the atoms,  $x$ , is equal to  $a$ . This correspondence between equations (4) and (14) is very useful because it will allow us to obtain  $W\beta$  from the surface stress and surface energy which can be measured or calculated. Similarly the energy change due to the presence of the substrate, which we call the soliton formation energy, is given by

$$U_2 + U_3 = (2/\pi) \sqrt{2\mu a^2 W} = W\alpha \quad (15)$$

with this equation serving to define the dimensionless parameter  $\alpha$ . Note that  $\alpha$  is always positive but that  $\beta$  may have either sign (since for a real metal surface  $b < a$ ). Hence it is energetically favourable for the chain of atoms to create a single compressive soliton if the sum of equations (14) and (15) is less than zero, that is if  $W\alpha + W\beta < 0$ .

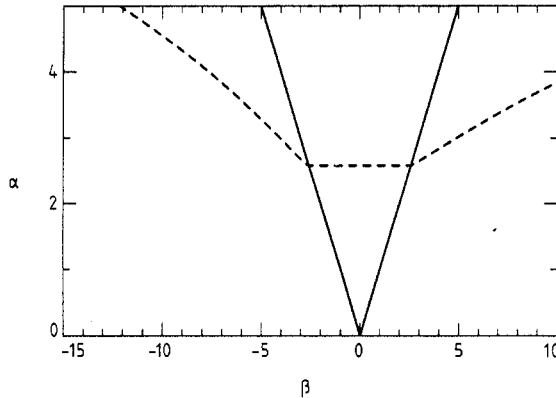
Similarly the energy to subtract a single atom from the chain, while keeping the separation of the atoms uniform, is

$$U_1 + \Gamma(N - 1) - U = -\Gamma - \frac{1}{2}\mu(a - b)^2 + \mu a(a - b) = -W\beta \quad (16)$$

and the formation energy for an expansive soliton is identical to the expression given in equation (15). This means that it is energetically favourable for the chain of atoms to create a single expansive soliton if  $W\alpha - W\beta < 0$ .

These two conditions give the criteria for contractive and expansive reconstructions respectively. The stability criteria can be restated in terms of the ratio  $|\beta|/\alpha$ ; if  $|\beta|/\alpha < 1$  then the unreconstructed surface is stable, otherwise it will reconstruct by adding atoms to the surface if  $\beta$  is negative and by subtracting atoms from the surface if  $\beta$  is positive.



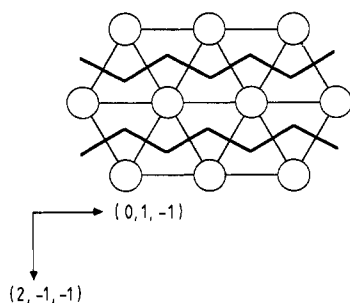


**Figure 2.** The phase diagram describing the reconstruction behaviour of the lowest energy equilibrium solution of the one-dimensional Frenkel–Kontorova model. The two straight lines  $\alpha = -\beta$  and  $\alpha = \beta$  divide the parameter space into three regions. In the region to the left the chain reconstructs compressively, in the region to the right it reconstructs expansively and in the region in the middle it is stable to reconstruction. The broken curve gives our estimate of the borderline of the validity of the continuum approximation, above the broken curve the approximation is good and below it is poor.

If it is energetically favourable for the chain to form a single soliton of one type then it will continue to form more solitons of the same type until such time as the repulsive interaction between them balances the formation energy. Such a balance will always occur because the repulsive interaction between solitons increases as their density increases.

Figure 2 shows the reconstruction behaviour in  $(\alpha, \beta)$  space. We see that the phase diagram is divided into three regions by the two lines  $\alpha = -\beta$  and  $\alpha = +\beta$ ; in the region to the left the surface is compressively reconstructed, in the middle it is unreconstructed and in the region to the right it is expansively reconstructed. The general behaviour of the chain as a function of the parameters  $\alpha$  and  $\beta$  is easy to understand; for example reducing the magnitude of  $\Gamma$  corresponds to keeping  $\alpha$  fixed and decreasing  $\beta$  which moves the representative point towards the left of the diagram where the tendency is for the surface to contract. This happens because a reduction in  $\Gamma$  results in a lower energy cost for adding atoms to the surface which favours compressive reconstructions.

We have used the continuum form of the Frenkel–Kontorova model and must investigate whether this is valid for a real surface. Bak (1981) has demonstrated that solutions of the discrete model show the same general features as solutions of the continuum version in the limit of small  $W$  and we need to decide whether this limit is applicable to our situation. The continuum approximation will certainly be poor if the first term that is neglected in the expansion of the left-hand side of equation (7) has the same magnitude as the term retained on the left hand side of equation (8). To illustrate this we have drawn a dotted line on the phase diagram of figure 2 corresponding to the  $(\alpha, \beta)$  pairs for which the ground state solution is such that the magnitude of the first term that is neglected in the continuum approximation is the same as the term retained on the left hand side of equation (8). Above the broken curve in figure 2 the continuum approximation works well whereas below it it is poor. Generally speaking, for small values of  $\alpha$  the continuum approximation is not valid. As  $\alpha$  is essentially the ratio of the strength of the surface springs to the strength of the substrate potential we can understand why this is; if  $W$  is large enough then we can expect solutions in which the atoms are pinned to the minima



**Figure 3.** A close-packed monolayer showing the zig-zag paths referred to in the text. The circles indicate the positions of the atoms of the substrate.

of the substrate potential. Continuum theory cannot hope to model these situations. In fact, it turns out that for the region of  $(\alpha, \beta)$  parameter space which applies for real surfaces the continuum limit is a very good approximation. We should note that, in the limit as  $W$  tends to zero, the simple model of section 2 is recovered since  $W\alpha$  tends to zero and the unreconstructed surface is unstable to adding atoms if  $W\beta$  (which is independent of  $W$ ) is negative and unstable to subtracting atoms if  $W\beta$  is positive.

We point out that the criteria we have derived in this paper are similar to those of Frank and van der Merwe (1949) but differ in that  $W\beta$  includes two extra terms absent in their work: (i)  $\Gamma$  and (ii)  $\frac{1}{2}\mu(a-b)^2$ . The first term is present because  $\Gamma$  was introduced as an additional parameter that we argued was necessary in the theory of surface reconstructions and the second is present because our derivation is equivalent to minimising the energy per unit length of the surface and *not* the energy per atom as was done by Frank and van der Merwe (1949). Our minimisation is the appropriate one for the theory of surface reconstructions but in fact for real surfaces  $(a-b)/a$  is small so that this second term is probably not an important factor in determining whether a surface will reconstruct or not. We do, however, believe that this difference is conceptually important because it is only with our formulation that one can directly link the energy cost to add an atom to the surface,  $\Delta E$  or  $W\beta$ , with the surface stress and surface energy via equations (4) and (14).

## 5. Choice of parameters

In this section we discuss the values of the parameters that are appropriate for real close-packed metallic surfaces. Of course real surfaces are two-dimensional and our model is only one-dimensional, this is a severe limitation of our approach but we can still discuss the stability of surfaces against reconstructions which involve essentially one-dimensional rearrangements of the atoms. Because reconstructions of the type discussed here are rare we expect our analysis to indicate that the unreconstructed surface is stable in most cases. In fact the  $23 \times \sqrt{3}$  reconstruction of the close-packed gold (111) surface undergoes a reconstruction which appears to involve the insertion of an extra row of atoms into the surface every 23 rows (Harten *et al* 1985), which is essentially a one-dimensional rearrangement of atoms. In order to apply our model we map the real two-dimensional surface problem onto a one-dimensional chain model. To do this we follow the idea of El-Batanouny *et al* (1987) and consider the zig-zag path connecting inequivalent stacking sites on the (111) surface to be unfolded (or straightened out) into a one-dimensional line (see figure 3). We then apply the one-dimensional Frenkel–Kontorova model to the atoms along this line. This is not an exact mapping but we believe that, because of the simple nature of the ball and spring model and the uncertainty in the appropriate values of the parameters, a more sophisticated approach is not warranted.

Let us consider the form of the substrate potential along the unfolded zig-zag path of figure 3. The stacking of close-packed layers is ABC for a face-centred-cubic structure so that on the unreconstructed (111) surface there are two inequivalent stacking sites that an atom can occupy at which the substrate potential will have minima. For the real surface these two stacking sites will have different energies, and we could include this in our model by representing the substrate potential by its first two Fourier components (as was done by El-Batanouny *et al* 1987) and then solving the Frenkel–Kontorova model for this new potential. However we do not use this approach since we expect the energy difference between the two stacking sites to be small compared with the overall height of the substrate potential. There is experimental evidence to support this; Wang and Ehrlich (1989) found that the barrier height to single atom diffusion on the Ir (111) surface is nearly 20 times the energy difference between the two inequivalent stacking sites. We would expect this general picture to remain true for a whole surface layer of atoms sliding over an underlying substrate. This observation implies that the second Fourier component of the substrate potential along the zig-zag path is much larger than the first. In addition El-Batanouny *et al* (1987) interpreted the experimental diffraction data of Harten *et al* (1985) as implying that the second Fourier component for the Au(111) surface is 100 times larger than the first. In light of these observations we will consider a model in which the substrate potential along the zig-zag path is modelled by taking only its *second* Fourier component, and where adjacent atoms in the *unreconstructed* chain occupy troughs of the substrate potential which correspond to the bulk FCC stacking sites. This means that between any two adjacent atoms in this chain there is an empty trough in the substrate potential corresponding to the alternative (HCP) stacking site (in the single sine model that we study here, the two alternative sites will naturally be degenerate in energy). This results in a simple modification of the analysis of sections 3 and 4: the position of atom  $n$  is written as  $x_n = au_n + 2an$  rather than  $x_n = au_n + an$  to make it clear that the separation of nearest neighbours in the unreconstructed surface is  $2a$  rather than  $a$ . The same analysis then follows; in particular the reconstruction criteria derived in section 4 are unchanged apart from the replacement of the constant  $a$  in equations (11) to (16) by  $a' = 2a$  (the *true* periodicity of the zig-zag path on the (111) surface).

Now we discuss the values of the model parameters  $a'$ ,  $b$ ,  $\mu$ ,  $W$ , and  $\Gamma$  that are appropriate for the zig-zag path on the (111) surface that we mentioned earlier. We will apply the model to the four metals aluminium, iridium, platinum and gold. First of all we can deal very quickly with the parameter  $a'$  because it is simply the distance between two equivalent FCC stacking sites along the zig-zag path on the (111) surface.

We have estimated the values of the surface force constants,  $\mu$ , by using a nearest neighbour expression for the bulk modulus of the materials. In fact force constants at surfaces can differ markedly from their counterparts in the bulk, but rather little is understood about this at the moment. Because surface atoms have fewer neighbours than bulk atoms one would think that the remaining surface bonds would be stronger and presumably stiffer than those in the bulk. However, the surface bonds are stretched from their equilibrium lengths and this will tend to make them softer. Investigations of the (111) surfaces of noble metals, for example the work of Doak *et al* (1983) and Bortolani *et al* (1984a) on silver and Bortolani *et al* (1984b) on gold, appear to indicate that the surface bonds are softer than those in the bulk. On the other hand work on aluminium surfaces has indicated that in this case the surface force constants are nearly the same as those in the bulk. Because of these difficulties we use a crude estimate based on bulk quantities. We must be careful to use the spring constant appropriate to the

atomic displacements that we are considering, i.e. the spring constant for displacing lines of atoms in the direction of the zig-zags. The appropriate spring constant for the one-dimensional Frenkel–Kontorova model is then given by  $\mu = 3\mu'/2$  where  $\mu'$  is the spring constant for a single bulk bond.

$W$  is the amplitude of the sinusoidal substrate potential. Accurate values for this quantity are not available but we believe that it is very small. Goodwin *et al* (1989) have calculated the energy to slide close packed layers of aluminium over one another. From their results we can estimate that, for aluminium, the amplitude of the substrate potential is of the order of 0.1 eV. In addition experimental measurements show that the activation barriers for diffusion of single atoms at surfaces is of a similar magnitude (see for example Wang and Ehrlich (1989)). Although these estimates of  $W$  are rather crude we believe that all the available evidence points to values for  $W$  of the order of 0.1 eV, and this is the value we shall use for each of the four metals studied here. It would be interesting to perform energy calculations to determine the size of  $W$  more accurately.

This leaves the parameters  $\Gamma$  and  $b$ . We can bypass the problem of knowing this pair directly by following the argument given in section 2 of this paper concerning the energy change on adding an atom to the surface layer. We then extend this argument to the two-dimensional (111) surface by considering the zig-zag paths mentioned earlier. Consider a chain of  $N$  atoms connected by nearest neighbour springs but lying on a smooth substrate; this leads to the Frenkel–Kontorova model with  $W = 0$  which was considered in section 2 of this paper. We suppose that the chain has total length  $L$  and all of the atoms are equally spaced with separation  $a'$  so that the energy of this chain is given by equation (1) with  $x = a'$ . Equations (4) and (14) imply that the energy change,  $\Delta E$ , on adding an extra atom to the surface layer is given by

$$\Delta E = \Gamma + \frac{1}{2}\mu(a' - b)^2 - \mu a'(a' - b) = a'(\gamma_{1D} - g_{1D}) = W\beta \quad (17)$$

where  $\gamma_{1D}$  and  $g_{1D}$  are the one-dimensional surface energy and stress respectively and we have noted that  $\Delta E$  is equal to  $W\beta$  (note that  $W\beta$  does *not* depend on  $W$ ). We shall use numerically computed values for the surface stress and surface energy calculated for the unreconstructed two-dimensional surface to give values for the parameter  $W\beta$  for the four metals we study here. It should be noted that the substrate potential *is* present in the computations which lead to the values for the stress and surface energy that we use, whereas equation (17) was derived assuming that  $W$  is zero.

Equation (17) is written in terms of the quantities  $\gamma_{1D}$  and  $g_{1D}$  which are appropriate for a one-dimensional chain, whereas we want to use quantities calculated for two-dimensional surfaces. Therefore we must decide how to modify equation (17) by considering the zig-zag paths on the close-packed (111) surface (see figure 3):

(i) a distance corresponding to the periodicity of the substrate potential along the zig-zag path (in other words the length of two of the straight line portions in figure 3) is equivalent to the two dimensional surface area per atom. Hence  $a'\gamma_{1D}$  in equation (17) should be replaced by  $A_{\text{atom}}\gamma_{2D}$  where  $A_{\text{atom}}$  is the surface area per atom on the unreconstructed surface and  $\gamma_{2D}$  is the surface energy per unit area.

(ii) by making a cut through the zig-zag paths in figure 3 in the  $(2, -1, -1)$  direction we can equate the average one-dimensional line stress across this cut with the two-dimensional stress (which is isotropic for the unreconstructed close-packed surface) multiplied by the length of the cut. This implies that  $g_{1D}$  should be replaced by  $\sqrt{3}a'g_{2D}/2$ , where  $g_{2D}$  is the two-dimensional surface stress and  $a'$ , as before, is the periodicity of the substrate potential along the zig-zag path. With these modifications equation (17) becomes

$$W\beta = A_{\text{atom}}(\gamma_{2D} - \frac{1}{2}\sqrt{3}g_{2D}) \quad (18)$$

and so knowledge of the two-dimensional surface stress and energy gives  $W\beta$  directly.

**Table 1.** The values of the model parameters for aluminium, iridium, platinum and gold (111) surfaces.

	$W\beta$ (eV)	$a'$ (Å)	$\mu$ (eV Å <sup>-2</sup> )	$W$ (eV)	$\alpha$	$\beta$
Al	-0.31	3.31	2.91	0.1	16.1	-3.1
Ir	-1.51	3.12	13.56	0.1	32.3	-15.1
Pt	-2.20	3.20	10.85	0.1	30.3	-22.0
Au	-1.10	3.33	7.02	0.1	25.0	-11.0

The values of the parameters  $W\beta$ ,  $a'$ ,  $\mu$ ,  $W$ ,  $\alpha$  and  $\beta$  that we have obtained for the close-packed surfaces of aluminium, iridium, platinum and gold, using the arguments of this section, are given in table 1. The values of  $\alpha$  were obtained from the values of  $a'$ ,  $\mu$  and  $W$  using equation (15) (remembering to replace  $a$  by  $a' = 2a$ ) and the values of  $W\beta$  from equation (14) using the values for  $g_{2D}$  and  $\gamma_{2D}$  calculated by Needs and Godfrey (1990) and by Needs and Mansfield (1989).

## 6. Stability of the close-packed surfaces

In this section we discuss the application of the Frenkel–Kontorova model to real metallic (111) surfaces. First of all we can use the values of  $\alpha$  and  $\beta$  to determine whether the continuum limit is a good approximation to the discrete Frenkel–Kontorova model for these surfaces. Using the values given in table 1 we can see that the appropriate points ( $\alpha$ ,  $\beta$ ) are well above the dotted line in figure 2 and hence we are in the regime where the continuum limit is an excellent approximation to the discrete model.

The values of  $\alpha$  and  $\beta$  given in table 1 place all four metals in the region where the surfaces do not reconstruct (the appropriate points are not in the region of ( $\alpha$ ,  $\beta$ ) space that is plotted in figure 2). The aluminium surface is predicted to be very stable against reconstruction while the iridium, platinum and gold surfaces are much closer to being unstable against reconstructions which increase the density of surface atoms. Because  $W\beta$  is negative in each case, reconstructions involving a decrease in the density of surface atoms are extremely unlikely. Our model differentiates strongly between the nearly-free-electron metal aluminium and the transition and noble metals iridium, platinum and gold. However, the values of  $\alpha$  and  $\beta$  for the three transition and noble metals are quite similar. In fact the surface structures of iridium, platinum and gold are somewhat similar (Van Hove *et al* 1981 and references therein), and prediction of similar behaviour for the surfaces of these materials is a significant success for our simple model.

Although the close-packed surfaces of metals do not in general reconstruct, in agreement with our model, the gold (111) surface in fact does so. The gold (111) surface forms a  $23 \times \sqrt{3}$  reconstruction which appears to consist of the insertion of an extra row of atoms every 23 rows. This structure can thus be viewed as an essentially one-dimensional reconstruction. We believe that this reconstruction is an example of an instability of the general type that we have discussed in this paper. Our simple model does not predict this reconstruction but presumably both the model and our knowledge of the appropriate values of the parameters are too crude to correctly reproduce the differences between the iridium, platinum and gold.

The appropriate values of the model parameters are not well known and we wish to encourage others to calculate them more accurately. There are a number of improvements which could be made, for instance the understanding of surface force constants is progressing rapidly and experiments so far performed have indicated that the bonds at

the gold (111) surface (Doak *et al* 1983) may be between 30% and 50% softer than in the bulk. Note that  $W\alpha$  would decrease if the surface force constant,  $\mu$ , were decreased but our estimate of  $W\beta$  would remain *fixed* because we obtain it from calculations of the surface energy and surface stress which implicitly include the bond softening effect. Inclusion of the bond softening effect in  $W\alpha$  would mean that the gold surface is closer to the instability towards increasing the surface density of atoms than our crude estimates suggest. Another important effect is that the substrate interaction parameter  $W$  may be very small for gold because it has a full 5d shell so that directional bonding forces are less important than in iridium or platinum. Again this would tend to make the surface unstable and these two reasons, the bond softening and the relatively weak substrate interaction, may tip the balance in favour of an instability for gold.

## 7. Conclusions

In conclusion, we have used the continuum form of the Frenkel–Kontorova model, including an energy cost term for each atom, as a simple model for the surface layer of a crystal. Whether or not the surface is stable against reconstruction is the outcome of competition between the tendency to change the density of surface atoms and the disruption of the bonding that such a reconstruction would entail. We have shown that the stability of the unreconstructed surface depends on the ratio of two dimensionless parameters  $\alpha$  and  $\beta$  which have simple physical interpretations. Our derivation has shown that the parameter  $\beta$  is related to the surface energy and surface stress; quantities which can be measured or calculated for a real surface.

The minimum energy reconstructed solutions are periodic arrays of dislocations or solitons. These solutions form part of a general class of surface reconstructions where the density of surface atoms is either increased or decreased from the substrate density. The model has been applied, with suitable choices for these parameters, to the close-packed (111) surfaces of the fcc metals gold, platinum, iridium and aluminium. The uncertainties in the appropriate values of the parameters are quite large but some qualitative conclusions can be drawn from this analysis. Our model indicates that the (111) surfaces of gold, platinum, iridium and aluminium should not reconstruct, which is incorrect for gold but correct for the other surfaces. Our model predicts similar behaviour for the surfaces of gold, platinum and iridium (which is on the whole in agreement with observations) but that aluminium should behave in a rather different fashion. We find that expansive solutions, where the density of surface atoms is reduced, are extremely unlikely. On the other hand contractive solutions, in which the surface density of atoms is increased, are possible for real metallic surfaces.

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