A two-component Frenkel–Kontorowa model for surface alloy formation

Istvan Daruka[1] **and J C Hamilton**

Sandia National Laboratories, MS 9161, PO Box 969, Livermore, CA 94551-0969, USA

Abstract

It has been shown by recent experiments that bulk immiscible metals (e.g. Ag/Cu, Ag/Co and Au/Ni) can form binary alloys on certain surfaces where the substrate mediates the elastic misfits between the two components, thus relieving the elastic strain in the overlayer. These novel surface alloys exhibit a rich phase structure. We formulate a two-component Frenkel–Kontorova model in one dimension to study surface alloy formation. This model can naturally incorporate dislocation formation that plays a crucial role in determining the actual structure of the system. Using energy minimization calculations we provide a phase diagram in terms of average alloy composition and the energy of mixing. Monte Carlo simulations were also performed to study the structure and interaction of the emerging dislocations.

Recent experiments have shown that bulk immiscible metals such as Ag/Cu [1] (see figure 1), Ag/Co [2], Au/Ni [3, 4], Ag/Pt [5], Co/Ag [6] and Fe/Ag [6] can form alloys if deposited as a thin film on top of a substrate. In these examples the substrate mediates the elastic misfit between the constituents of the adlayer leading to a balance between the elastic and chemical interactions. Due to the competition between the elastic and chemical effects a rich variety of morphologies can form. Experimentally observed morphologies include pseudomorphic domain and striped structures [2, 3, 6], dislocation formation [7], coexistence of dislocations with pseudomorphic structures [1, 2], and phase separation where there is no surface alloying [7, 8]. These novel, self-organized surface alloy structures offer amenable features for several electronic and magnetic nanoscale device applications as well as for catalysis.

There are several theoretical approaches aimed at understanding the thermodynamics of surface alloy formation. Continuum elasticity models have been developed by Ng and Vanderbilt [9], Vanderbilt [10] and Marchenko [11] to describe possible surface alloy phases. Tersoff [12] formulated a harmonic lattice model for surface alloying in immiscible systems. A first-principles approach combined with an effective model was presented to study the short-range order and phase stability in the Pd/Au system on Ru(0001) [13]. Another

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[1] Present address: Department of Theoretical Physics, University of Debrecen, PO Box 5, H-4010 Debrecen, Hungary.
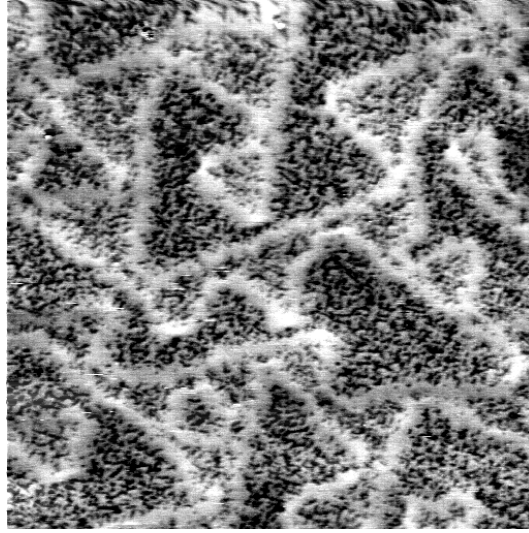
Figure 1. An STM image of a one monolayer thick Ag/Cu film deposited on a Ru(0001) substrate with an atomic fraction $X_{Cu}/X_{Ag} = 0.42$ [1]. The bright regions are made of silver atoms forming a pronounced network of dislocations. These dislocations separate pseudomorphic domains of the Ag/Cu alloy phase.

approach combined first-principles techniques with Monte Carlo simulations to characterize the emerging structures in the experimentally investigated Ag/Co on Ru(0001) system [14, 15]. Krack *et al* [16] used a lattice-model Hamiltonian to describe the emerging pseudomorphic structures in bulk immiscible alloy films. Fomin [17] and Fomin and Shantsev [18] used perturbative techniques to study a generalized continuum Frenkel–Kontorowa (FK) model for solid solutions. In general, the existing theoretical approaches provide an accurate description of the possible pseudomorphic surface alloy structures, but they do not address properly the formation, structure and properties of the dislocations ubiquitous in surface alloy systems.

In this paper we formulate a discrete, two-component FK model to study surface alloys. The merit of this approach is that it naturally incorporates dislocation formation. Due to the richness of the physics that the conventional one-dimensional FK model exhibits [19], and also to keep our problem numerically tractable, we perform our investigations in one spatial dimension. We consider a finite, one-dimensional chain of two types of atoms, A and B, deposited on top of a rigid substrate. Each atom interacts with its two nearest neighbours via harmonic springs and also with the substrate represented by a cosine interaction potential. We also include an additional energy of mixing term E_{AB} between the A and B type atoms. Thus, the total energy of the system can be described as

$$E = \sum_i \left\{ \frac{1}{2} K (x_{i+1} - x_i - a_i)^2 + \frac{1}{2} V \left(1 - \cos\left(\frac{2\pi}{b} x_i \right) \right) + E_{AB} \delta_{Ai} \delta_{B(i+1)} \right\}$$

where b is the lattice constant of the substrate and a_{AA}, a_{BB} and a_{AB} are the equilibrium bond lengths of the AA, BB and AB bonds, respectively. For simplicity, we assumed above that neighbouring atoms interact via the same harmonic potential described by one spring constant K. In addition, we include an interaction with the substrate described by a cosine potential with an amplitude V. Finally, we choose the bond lengths as $a_{AA}/b = 1+\varepsilon$, $a_{AB} = b$, $a_{BB}/b = 1-\varepsilon$. This way the amplitude of the compressive and tensile misfit (ε) between the equilibrium bond lengths will be the same. We note that this model is a natural generalization of the extensively

studied one-component FK model. The above two-component model can easily be generalized to two spatial dimensions and/or can also accommodate atom-type-dependent interactions. Next we scale the energy $E \rightarrow e = E/Kb^2$, the substrate potential $V \rightarrow v = V/Kb^2$ and the energy of mixing $E_{AB} \rightarrow e_{AB} = E_{AB}/Kb^2$. After scaling, we are left with four parameters in the model: the composition of the A type of atoms $c = N_A/(N_A + N_B)$, the lattice misfit ε, the substrate potential v, and the chemical interaction energy e_{AB}. N_A (N_B) denotes the number of A (B) atoms in the system. For our investigations we fix $v = 0.002$ and $\varepsilon = 0.075$. The value of the lattice misfit ε was chosen to match the experimental value that occurs in the Ag/Cu system deposited on Ru(0001) [1].

In the one-dimensional one-component FK model at zero temperature the morphology is determined by the ratio $r = \varepsilon^2/v$ [20]. For $r < r_c = 16/\pi^2$, there is a pseudomorphic, commensurate phase where each atom occupies the minima of the substrate potential. For $r > r_c = 16/\pi^2$, atoms will be displaced in some regions such that they gradually go through the maxima of the substrate potential as we proceed along the chain. We call these regions of disregistry dislocations. The width of the dislocations also depends on the ratio r. Because of the presence of dislocations, the atomic chain will be incommensurate with the substrate. This morphological transition is known as the commensurate–incommensurate transition [19]. The above choice of parameters v and ε in our model corresponds to the dislocated, incommensurate phase in the one-component FK model.

We determined the optimal, minimum energy dislocation widths for our parameters $v = 0.002$ and $\varepsilon = 0.075$ at compositions $c = 0$ and 1 as follows. We put a chain of n equally spaced atoms onto a substrate with a linear extension $(n - 1)b$ and $(n + 1)b$ for $c = 0$ and 1 respectively, and implemented a periodic boundary condition at the ends of the chain. Making use of the conjugate gradient method [21], the minimum energy per atom, e_d and the corresponding atomic positions were calculated for each value of n in the interval $3 \leqslant n \leqslant 30$. The $e_d(n)$ curves were identical for both cases $c = 0$ and 1 as one can expect by the symmetry of the total energy function E (equation (1)) with respect to the sign of the misfit ε. We found that the minimum energy dislocation configuration consists of $n = 14$ atoms per dislocation.

Next we turn to investigate the possible zero-temperature morphologies of the two-component FK system by constructing a phase diagram in terms of the remaining parameters: the composition c and the energy of mixing e_{AB}. Since we have a symmetric compressive and tensile misfit ε in the system and the corresponding elastic interaction is quadratic in the Hamiltonian (equation (1)), the phase diagram should be symmetric about $c = 0.5$. Consequently we only study the region $0 \leqslant c \leqslant 0.5$, i.e. when the B atoms are in majority in the system. We assume that the zero-temperature phases include dislocation-free pseudomorphic domains of A and B atoms that might coexist with the pure dislocated phase of the majority component B atoms. At zero temperature the system will occupy its lowest-energy state. Thus, for a given set of parameters (c, e_{AB}), the ground state structure can be determined by comparing the total energies of the possible configurations making use of the common tangent construction. In this way, repeating the common tangent construction for each e_{AB}, we can construct a zero-temperature (c, e_{AB}) phase diagram. However, in practice we are limited in the number of domain structures for which we can evaluate the energy. Thus, we restrict ourselves to a certain class of domain structures that we investigate. Making use of a conjugate gradient method we determine the minimum energy and the corresponding configuration of the n_1^A:n_2^B:n_3^A:n_4^B type periodic pseudomorphic domain structures in which n_1^A A atoms are followed by n_2^B B atoms, those are followed by n_3^A A atoms, and finally by n_4^B B atoms. We impose periodic boundary conditions on these structures and consider domain lengths (the number of atoms in the individual domains) between 1 and 20. This range of allowed domain sizes leads to 160 000 possible configurations at each value of e_{AB}.
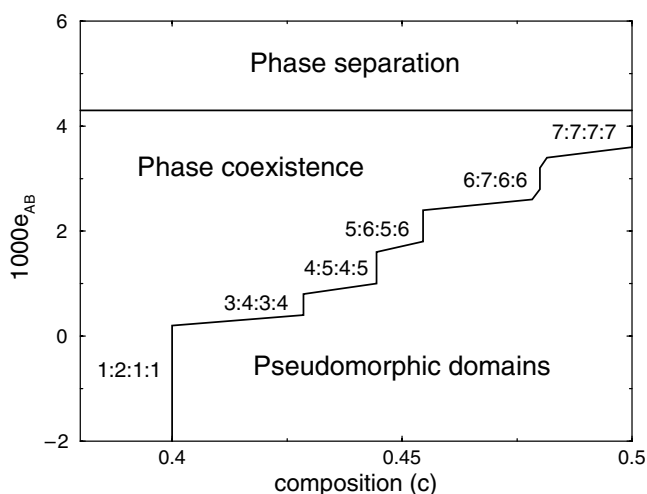
Figure 2. Phase diagram for a one-dimensional two-component FK model in terms of the alloy composition c and the energy of mixing e_{AB}. There are three phases present in the system: (i) phase separation, where no surface alloy forms; (ii) phase coexistence, where dislocations coexist with pseudomorphic domains; and (iii) pseudomorphic domains only. The lengths of the different n_1^A:n_2^B:n_3^A:n_4^B pseudomorphic domain structures that coexist with the dislocated phase at the corresponding phase boundary compositions are also indicated.

Making use of the above procedure we obtained the zero-temperature (c, e_{AB}) phase diagram shown in figure 2. We found three different morphologies in the system:

(i) *Phase separation.* For very large values of the repulsive energy of mixing, e_{AB}, it is energetically unfavourable to form A–B bonds and consequently the A and B type atoms phase separate in the system, forming two half chains. Both half chains correspond to a pure, one-component FK system. Also, the half chains contain dislocations since we are in the incommensurate phase of the corresponding one-component FK models.

(ii) *Phase coexistence.* At moderate values of e_{AB}, there is a phase coexistence between alternating pseudomorphic domains of A and B type atoms and dislocations made of the majority component B type atoms. The excess majority component B atoms that do not contribute to the pseudomorphic domains will form dislocated regions, the stoichiometry of which is determined by the common tangent construction. By forming a pseudomorphic domain structure, the system can relieve its elastic energy at the expense of the introduction of A–B bonds. The length of the pseudomorphic domains will depend both on the A–B bond energy e_{AB}, and on the composition c. At higher values of e_{AB}, the average domain length is larger in order to decrease the number of A–B bonds in the system. The corresponding n_1^A:n_2^B:n_3^A:n_4^B domain lengths that coexist with the dislocated phase at the corresponding phase boundary concentrations are also shown in figure 2.

(iii) *Pseudomorphic domains.* At small or negative values of interaction energy e_{AB} and at compositions close to $c = 0.5$ the system consists of pseudomorphic A–B domains only. The structure of the energy states of the investigated configurations suggests that the prevailing pseudomorphic domain structure exhibits a 'devil's staircase' character as a function of the alloy composition c. The devil's staircase nature of the pseudomorphic domains would imply that there are infinitely many ground states in this regime of the phase diagram. Each of these phases differs in the lengths of the corresponding pseudomorphic

A and B domains for different concentrations. Other, detailed studies (based on a lattice-model Hamiltonian approach) investigated this intriguing feature further and proved the existence of a complete devil's staircase structure for the pseudomorphic domains [16].

We expect that the structure of the derived phase diagram is quite robust and it mainly depends on the ratio $r = \varepsilon^2 / v$ [20]. For values $r > r_c = 16/\pi^2$ we expect the same topology, and for $r < r_c = 16/\pi^2$ we expect that the *'phase coexistence'* phase disappears due to the lack of dislocations. This latter assumption was confirmed by the findings of [16].

The above discussed phase structure reflects a competition between chemical interactions (implemented by the energy of mixing term e_{AB}) and elastic interactions. The repulsive chemical interactions favour phase separation in the system while the surface-mediated elastic interactions favour alloying. When chemical interactions are strong enough we get complete phase separation in the system, i.e. the system consists of two dislocated half chains. When the elastic interactions dominate, we get alloying, manifested by pseudomorphic domains. And when the magnitude of the two types of interactions in the system is comparable, we get phase coexistence between dislocations and pseudomorphic domains.

Even though we investigated a one-dimensional FK model, the derived zero-temperature phase diagram *qualitatively* captures many features of the experimentally observed surface morphologies of two-component systems. For example, the experiment of Stevens and Hwang [1] demonstrated that the bulk immiscible Ag and Cu deposited on Ru(0001) forms a surface alloy for small Cu concentrations coexisting with the majority component dislocated Ag phase. This morphology corresponds to the *phase coexistence* (ii) phase of our phase diagram. Phase coexistence between an alloy domain structure and a dislocated phase has been observed in many other bulk immiscible surface systems, such as Ag/Co on Ru(0001) [2], Au/Ni on Ni(110) [4] and Ag/Pt on Pt(100) [5]. As we change the relative concentration of the constituent surface atoms, other structures might emerge: at smaller Au concentrations on Ni(110) a non-dislocated surface alloy forms [3]. This latter case and the pseudomorphic lateral stripes observed in the Co/Ag and Fe/Ag on Mo(110) systems [6] correspond to the *pseudomorphic domains* (iii) phase in our phase diagram. Experimental examples for the *phase separation* (i) phase include the Ag on Ru(0001) system, where the Ag phase is dislocated [7], and the Co on Ru(0001) system, where the Co phase is pseudomorphic [8].

The above-discussed phase diagram describes the possible morphologies that the investigated system can exhibit at zero temperature. On the other hand, in order to understand the thermodynamics of this two-component system and to investigate the emerging structures at finite temperatures, we have performed Monte Carlo simulations. In principle, a state of the system can be characterized by the positions of each atom along the one-dimensional chain, $\{x_i\}$ and the type of atom along the chain, $\{c_i = A, B\}$. The total energy of the system in the state $\{x_i, c_i\}$ can be obtained by equation (1). However, due to the enormous number of local energy minima the system exhibits ($\approx 2^{200}$ for a chain containing 100 A and 100 B type atoms) it is computationally prohibitive to perform continuum space Monte Carlo simulations. Thus, to keep our problem numerically tractable we have discretized the states of the system as follows. We have introduced a discrete grid on the position space of the atoms $\{d_i\}$, such that $d_1/b = 0$, $(d_{i+2} - d_i)/b = \{1, 2, 3\}$ and $(d_{i+1} - d_i)/b = \{0.5, 1, 1.5\}$. Here d_i is the discretized position of the ith atom ($1 \leqslant i \leqslant n$) along the chain, n is the number of atoms in the system and b is the lattice constant of the substrate. Next we assigned an energy E_{dc} to each $\{d_i, c_i\}$ configuration making use of the conjugate gradient method as follows. Using a starting configuration $\{d_i, c_i\}$ we employed the conjugate gradient method to find the corresponding local energy minimum of E_{dc} (equation (1)) in the continuous $\{x_i\}$ position space. Consequently, the discretized states of the system can be characterized by

$\{d_i, c_i, E_{dc}\}$. One might suppose that with the above discretization we could potentially lose some of the metastable states of the continuum model. To address this we have performed molecular dynamics simulations in the continuum model. We have annealed several $\{d_i, c_i\}$ configurations at high enough temperatures and then quenched them by taking away the kinetic energy of the particles at each time step (kinetic annealing). The *same* local energy minima were revealed both by the discretized Monte Carlo and by the molecular dynamics simulations justifying the above discretization procedure. We have implemented a Metropolis algorithm (see e.g. [22]) to update the $\{d_i, c_i, E_{dc}\}$ configurations. In particular, in one simulation step we interchanged two subdomains to generate a trial configuration of $\{c_i\}$ and left the discretized atomic positions $\{d_i\}$ unchanged, while in the consecutive simulation step we left the atomic configuration $\{c_i\}$ unchanged and changed only the atomic positions $\{d_i\}$.

For our simulations we studied chains comprising up to 300 atoms with free chain ends. Most of our simulations were performed at a scaled temperature $t = k_B T / K b^2 = 0.0002$, where k_B is the Boltzmann constant, K is the spring constant, and b is the lattice constant of the substrate. We have monitored the following quantities: total elastic energy, total energy of mixing, total energy, domain size distribution, number of dislocations, and the position of the dislocation cores. In order to compare the finite-temperature morphologies to the zero-temperature structures, several phase points of the (c, e_{AB}) phase diagram were studied. For each of these points, we carried out two runs, with two different initial conditions. In the ordered start, the A and B atoms were arranged phase separated to form two domains, while in the disordered start the A and B atoms were distributed randomly. In general, the phase structures obtained from the finite-temperature Monte Carlo simulations agreed well with the predictions of the zero-temperature phase diagram and the resulting structures were insensitive to the investigated chain lengths (40–300 atoms). The corresponding domain sizes obtained by the Monte Carlo calculations were in quantitative agreement with the values derived from the zero-temperature phase diagram. However, in some cases the domain structure and dislocation number were found to be somewhat different for the ordered and disordered starts. We attribute this difference to the presence of degenerate structures with almost identical total energy but with significantly different energy of mixing and elastic energy contributions due to the difference in domain structure. Such degenerate structures were explicitly revealed by the Monte Carlo simulations.

Furthermore, the Monte Carlo simulations enabled us to study the structure and properties of dislocations. We locate the core of a dislocation by finding the position of the atom of which the substrate potential $1 - \cos(2\pi x_i / b)$ has a maximum, and define the width of the dislocation as the number of atoms located between the nearest positions of atoms of which $1 - \cos(2\pi x_i / b)$ has a minimum. We have found that the dislocations comprised 14 atoms. This number coincides with the dislocation widths derived from the above-discussed energy minimization calculations for the pure, one-component FK chains using the conjugate gradient method.

We also investigated whether there is a tendency to ordering at the dislocation core. To that purpose we calculated the probability of finding a B type atom at a separation of d atoms from the dislocation core. A typical result is shown in figure 3. The plot clearly shows that the dislocation core consists of only B type atoms. The revealed ordering in the vicinity of the dislocation core is not surprising if we consider that the effective misfit is biggest at such regions of the system. Thus, an atomic disorder/mixing would be energetically unfavourable around the dislocation core because it would introduce a surplus of elastic energy in the system. Such a decoration of dislocations by the majority components was also observed experimentally in the Ag and Cu system deposited on Ru(0001) [1] (see figure 1). In that system a pronounced network of dislocations forms at a certain range of Ag and Cu compositions and the dislocations are made of the majority component silver atoms, in agreement with our Monte Carlo result.
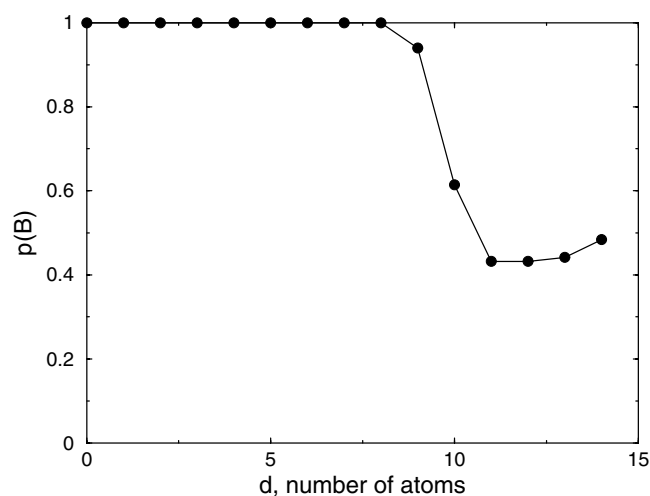
Figure 3. A typical plot showing the probability distribution $p(B)$ of finding a B atom at a separation of d atoms from the dislocation core. This result was obtained by a Monte Carlo simulation for a 200-atom chain containing 50 A and 150 B type atoms. The plot clearly demonstrates that the core of the dislocation consists purely of the majority component B type atoms. The energy of mixing parameter was set to $e_{AB} = 0.003$.

In order to obtain information about the interaction between dislocations we recorded the positions of the dislocation cores in the system as a function of the simulation step (see figure 4). Since we performed equilibrium Monte Carlo simulations we cannot identify the simulation steps with physical time, therefore the curves of the dislocation positions cannot be considered as physical trajectories. However, the random character of the core positions as demonstrated by figure 4 indicates that the interaction between the dislocations is relatively weak compared with the thermal disorder. The interaction between the dislocations was further studied by energy minimization calculations using the conjugate gradient method. We considered a finite chain with free ends and inserted two 15-atom wide dislocations comprising only B atoms. One of the dislocations was fixed at one end of the chain and the other one was moved through the chain such that the number of A–B bonds was conserved in the system. This way the total energy of mixing will be constant in the system and consequently the following results are independent of the energy of mixing parameter e_{AB}. The rest of the chain consisted of a pseudomorphic, alternating sequence of individual A and B type atoms. The calculated interaction potential of the two dislocations separated by s atoms is shown in figure 5. We found that the interaction between dislocations is repulsive and to a good approximation it decays exponentially with the dislocation separation. The amplitude of the interaction was characterized by the energy difference ΔE between the configurations where the two dislocations touch each other and where they are very far apart. The obtained value $\Delta E/Kb^2 = 0.000\,15$ is smaller than the amplitude of thermal noise at the studied temperature $k_B T/Kb^2 = 0.0002$, where K is the spring constant, b is the lattice constant of the substrate, T is the temperature and k_B is the Boltzmann constant. This relation supports our finding that dislocations do not order at the studied temperature in the Monte Carlo simulations.

Finally, we studied the effects of temperature on domain structure with the help of Monte Carlo simulations. We calculated the domain size distribution at temperatures $k_B T/Kb^2 = 0.0002, 0.0005, 0.001, 0.002$ and 0.01 and the corresponding normalized domain size curves for the B type atoms are plotted in figure 6. The results demonstrate that due to entropy
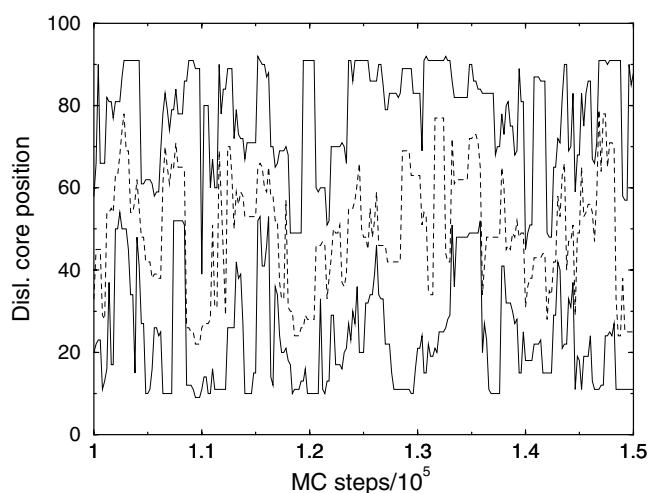
Figure 4. The positions of three dislocation cores along the one-dimensional chain as a function of the Monte Carlo simulation steps. The figure demonstrates that the positions of the dislocation cores are disordered at the temperature $k_B T / K b^2 = 0.0002$. The studied 100-atom chain contained 23 A type and 77 B type atoms and the energy of mixing parameter was set to $e_{AB} = 0.0005$.
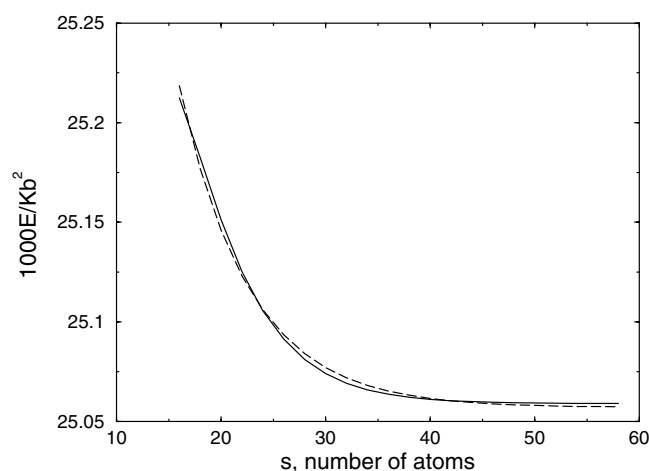

Figure 5. The total energy (E) of a one-dimensional FK chain containing two dislocations separated by s atoms (full curve). One dislocation was fixed at one end of the 100-atom chain and the other dislocation was moved through the chain. Both dislocations consisted of 15 B type atoms and the rest of the chain was a pseudomorphic ABAB domain structure. The dashed curve represents an exponential fit to the total energy curve: $1000 * E / K b^2 = 1.751 * \exp(-0.149 * d) + 25.057$. The energy difference between the two configurations where the two dislocations touch each other and where they are very far apart is $\Delta E / K b^2 = 0.000\,15$.

effects the average domain size decreases with increasing temperature, and at high enough temperatures atomic mixing is preferred as indicated by the strictly monotonically decreasing size distribution curves for $k_B T / K b^2 \geqslant 0.002$.

In summary, we have investigated a two-component FK model for surface alloy formation. We proposed a zero-temperature phase diagram in terms of the alloy composition c and the
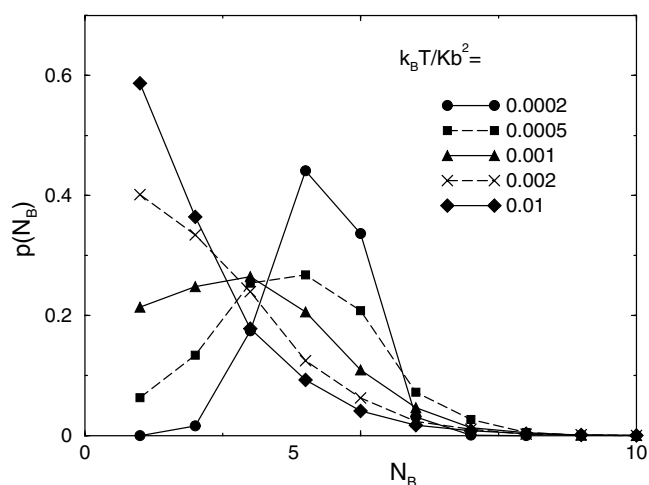
Figure 6. The temperature dependence of the pseudomorphic domain size distribution $p(N_B)$ for the majority component B atoms obtained by Monte Carlo simulations. We studied a chain containing 20 A type and 20 B type atoms and the energy of mixing parameter was set to $e_{AB} = 0.0015$ for these simulations. The average domain size decreases with increasing temperature. At high enough temperatures ($k_B T / K b^2 > 0.002$) atomic mixing is preferred as demonstrated by the two strictly monotonously decreasing curves for $k_B T / K b^2 = 0.002$ and 0.01.

energy of mixing e_{AB}. The resulting rich phase structure reflects the competition between the chemical and elastic interactions. The predicted structures include the main experimentally observed morphologies. The model also enabled us to study the structure and interaction of dislocations with the help of Monte Carlo simulations. In agreement with the experiments we have found that the dislocations are made of only the majority component atoms.

Acknowledgment

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