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## One dimensional model of strained epitaxy of a binary alloy

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(June 3, 2008)

We discuss the self-assembly of monatomic chains composed of atoms of two kinds on a periodic substrate. We assume that there exists small positive misfit between the average atomic diameter of the deposited atoms and the substrate lattice parameter. This may cause the chain size calibration. Our model calculations show that if the interatomic interactions are of ordering type, at low temperature the distribution of chain lengths at thermal equilibrium is more strongly peaked around the optimum length than in the case of chains composed from identical atoms.

**Keywords:** strained epitaxy; self-assembly; size distribution; monatomic chains; binary alloy; thermal equilibrium

### 1. Introduction

Controlled self-assembly and self-organization are expected to become major tools in nanoscale engineering [1]. One of the perspective technological processes is the self-assembly of size-calibrated islands taking place in some strained heteroepitaxial systems [2]. From the technological point of view, the goal is to grow structures with prescribed properties. However, our ability to control the growth is restricted to only indirect influences via the external conditions, such as the deposition flux, the substrate temperature, the coverage, etc. Therefore, it is important to thoroughly investigate all available possibilities of influencing the growth process.

In Ref. [3] for the case of one component deposit we showed that the ordered alloyed substrate can both facilitate the self-assembly and make the size distribution more narrow.

The aim of the present paper is to investigate how the size calibration is affected if the deposited material instead of the substrate is a mixture (or an alloy) of two atomic species. As in the above paper, we will study a one dimensional (1D) model which is useful not only as a simplest theoretical model to study the qualitative behavior in all dimensions, but is also of practical interest because 1D structures are being extensively studied to serve as nanowires [4] and atomic-scale magnets [5] for application in nanoscale devices. On the theoretical side, the simplicity inherent to 1D will allow us to use powerful analytical techniques [3, 6, 7].

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## 2. A simple model of misfit

To illustrate the physics of misfit let us consider the deposition of adatoms on a 1D periodic substrate. Assuming for simplicity that the adatoms are of the same kind, let us choose the substrate potential as in the Frenkel-Kontorova model

$$V_s(x) = k \left( 1 - \cos \frac{2\pi x}{a} \right), \quad (1)$$

where  $k$  is the strength of the potential and  $a$  the substrate lattice constant. The interatomic interaction between the adatoms is in general quite complex. In Ref. [8] we assumed that in the case of small misfit it can be treated in the harmonic approximation. This reduced the interaction to the nearest neighbor “chemical” part  $V_{NN}$  and to the harmonic part as in the Frenkel-Kontorova model.

In the present paper we further simplify this model by assuming that the spring constant of the interatomic harmonic interaction is very large which means that the adatoms interact as impenetrable spheres of some diameter  $d$ . The difference with the Frenkel-Kontorova model is that the atoms when in contact add to the system energy the (usually negative) “chemical” contribution  $V_{NN}$ .

Let us assume that there exists small positive misfit  $\Delta a \ll a$  between the adatom diameter  $d$  and the substrate lattice spacing

$$d = a + \Delta a \equiv a(1 + f), \quad (2)$$

where  $f$  is the relative misfit  $\Delta a/a$ . It is easy to show that in this model the energy of an atomic chain consisting of  $l$  adjacent atoms is

$$E_l = V^{NN}(l - 1) + k \left[ l - \frac{\sin(\pi l f)}{\sin(\pi f)} \right] \equiv E_l^{ch} + E_l^{el}, \quad (3)$$

where the first “chemical bond” term on the right hand side is the sum of interactions between nearest neighbor atoms and the elastic term

$$E_l^{el} = \sum_{i=1}^l V_s(x_i) \quad (4)$$

is due to the interaction with the substrate. The equilibrium positions of the atoms  $x_i$  in this equation are easily found from symmetry considerations.

The size calibration of the chains takes place when the reduced energy  $E_l/l$  has a global minimum as the function of  $l$  [7–9]. This case is illustrated by the solid curve in Fig. 1 corresponding to the misfit value  $f = 5\%$ . The oscillations on the reduced energy curves correspond to the appearance of the dislocations which in the presence of misfit and the are inevitable for rigid atoms in sufficiently long chains. We note that the global minimum of the solid curve corresponds to a coherent island. Coherent structures are considered to be more suitable for application in nanoelectronics because of their better quality. The dashed curve, however, does not have a global minimum at finite  $l$ . This means that if the misfit exceeds  $\sim 10\%$  the atoms tend to gather into dislocated chains with their length growing at diminishing temperature.

According to the approximate theory of Ref. [9] and to the exact solutions of

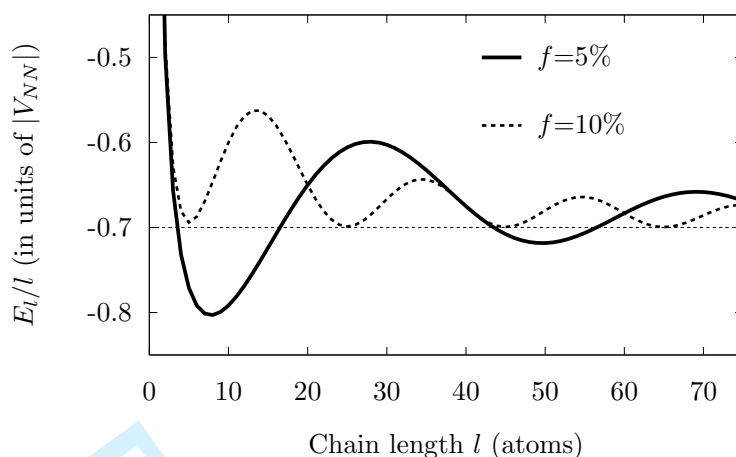


Figure 1. Reduced per atom energy of the chains of adsorbed atoms for two values of the misfit  $f$ . The substrate potential strength  $k$  in Eq. (1) was chosen to be equal to  $0.3|V_{NN}|$ . The horizontal line corresponds to the asymptotic value of  $E_l/l$  as  $l \rightarrow \infty$  [see Eq. (3)]. The dashed curve which passes above this curve does not have a global minimum at finite  $l$ .

Refs. [3, 7, 8], the size distribution of islands at finite temperature is

$$c_l \propto \exp\left(\frac{\mu l - E_l}{k_B T}\right), \quad (5)$$

where  $c_l$  is the concentration of islands of size  $l$  and  $\mu$  a parameter to fix the total coverage. From this equation it can be seen that at low temperature the size distribution is strongly peaked around the size corresponding to the global minimum of the reduced energy [9]. Furthermore, the very monomodal character of the distribution depends on the positive curvature of the function  $E_l$  in the vicinity of the minimum [10].

### 3. Equilibrium statistics of alloyed chains

As was noted in the Introduction, in 1D there is a lot of techniques for solving statistical problems exactly. At the heart of these techniques lies the transfer matrix method which is extremely efficient in the case of short-range interactions because it allows to reduce many-body statistical problems to the diagonalization of a transfer matrix of a size which is small in the case of short range interactions (e. g., the size is  $2^L$  in the binary alloy case where  $L$  is the radius of the interaction [15, Ch. II]). Elastic interactions, however, are not short range. For example, the chain energy of the form (3) can be shown to contain an infinite number of cluster interactions of the form

$$V_l p_{i+1} p_{i+2} \dots p_{i+l}, \quad (6)$$

where  $p_i = 0, 1$  is the occupation number of adatom on site  $i$  and  $V_l$  is the second discrete derivative of  $E_l$  [7]. Thus, if the nonlinear term in Eq. (3) is not of a polynomial type,  $V_l \neq 0$  for all  $l$ . In this case the transfer matrix has infinite size and the problem cannot be solved within conventional approach.

In Refs. [6–8], however, it was shown that Hamiltonians with interactions of the type of Eq. (6) are also exactly solvable and two methods for their solution were developed. In Refs. [3, 11] these methods were applied to the strained epitaxy

on alloyed substrates. Within these techniques the exact solutions were expressed through the chain energies  $E_l$  alone. The calculation of the partition function essentially consists in the counting of the configurations with a given distribution of the atoms between the chains of different lengths.

Our main observation in the present paper is that if (i) the elastic part of the energy of an alloyed chain is independent of the chain composition and (ii) the “chemical” interatomic interactions are restricted to the nearest-neighbor atoms then the elastic part factors out so that the statistical averaging within the chain can be performed by the usual means (see Appendix A for details).

The most speculative is, of course, the first of the above assumptions, i. e., that the elastic energy is independent of the chain composition. In terms of the simple model of section 2 this means that A and B atoms have the same diameter. While in general this may seem unrealistic, in many cases this can be a good approximation [12]. For example, according to Ref. [12] in the case of the CuAu system the empirical radii of the two atoms are identical. Thus, at least in some cases the above assumption is approximately fulfilled.

In Appendix A and below we show that the intrachain averaging over the alloy species amounts to effective introduction of chain energies  $E_l$  which formally enter into the formalism as the energies of a pure specie. This allows us to apply all the machinery developed for the pure case also in the alloy case.

To gain insight into the qualitative picture of the alloyed self-assembly, let us consider the simplest case of equiatomic alloy with the interatomic interactions between similar species being also equal (notation is explained in the Appendix):  $\mu^A = \mu^B$  and  $V^{AA} = V^{BB}$  which, in particular, means that  $a = c$  in Eq. (A2). According to Eq. (A10)

$$Z_{ch}^{(l)} = C \lambda_+^{l-1} \left[ 1 + \left( \frac{\lambda_-}{\lambda_+} \right)^{l-1} \right]. \quad (7)$$

This chemical part of the chain partition function can be formally expressed as corresponding to the following contribution into the chain energy

$$E_l^{ch(AB)}/k_B T = -(l-1) \ln \lambda_+ - \ln \left[ 1 + (\lambda_-/\lambda_+)^{l-1} \right] \quad (8)$$

which together with the elastic term can be substituted into Eq. (5) to find the size distribution. [In Eq. (8) we neglected a constant term which is irrelevant to our purposes.]

From the explicit expression for the T-matrix eigenvalues [see Eq. (A5)]

$$\lambda_{\pm} = e^{(\mu^{\alpha} - V^{\alpha\alpha})/k_B T} \left( 1 \pm e^{V/2k_B T} \right) \quad (9)$$

it is easy to see that depending on whether the ordering potential  $V$  in Eq. (A7) is positive (ordering case) or negative (phase separation case) the ratio of eigenvalues at lowering temperature will tend towards -1 or +1, respectively.

Let us first consider the second case ( $V < 0$ ). In this case from Eq. (9) is easy to see that the first, linear in  $l$  term in Eq. (8) at low  $T$  will correspond to the  $V_{NN} \simeq V^{\alpha\alpha}$  [ $\alpha = A$  or  $B$ ; we assume that the  $\mu^{\alpha}$  term will contribute to  $\mu$  in Eq. (5)]. This is rather natural because in the phase separation case atoms of different kinds are rarely found together and the majority of interatomic interactions is between the like atoms. The second nonlinear term may influence the shape of the size distribution [10]. However, because the ratio of the transfer matrix eigenvalues

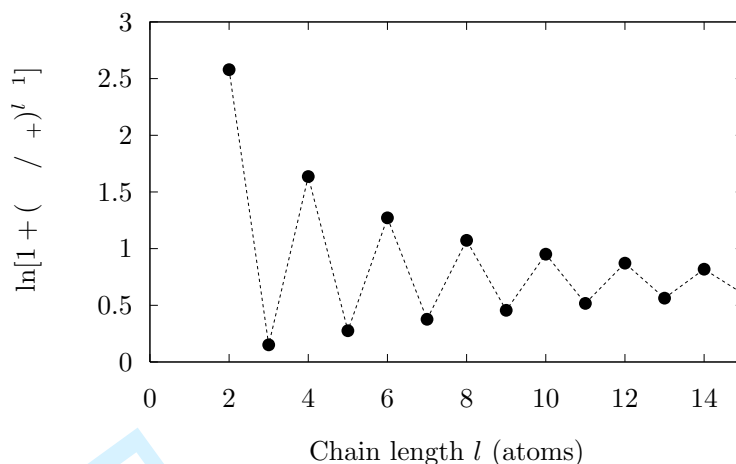


Figure 2. Non-linear in  $l$  contribution to the effective interaction Eq. (8) for alloyed chains of different length. For further explanations see the text.

tend to unity at small temperature, the nonlinearity weakens and its influence on the shape of the size distribution becomes negligible.

In contrast, in the ordering case ( $V > 0$ ) the nonlinearity grows with lowering temperature because the eigenvalue ratio tend to  $-1$ , so the amplitude of the oscillating term in Eq. (8) grows. This is illustrated in Fig. 2 where a moderate value  $\exp(-V/k_B T) = 5$  was chosen. The physical value of the potential would correspond at room temperature to  $V \simeq 0.13eV$ . Also from Eq. (9) it is easy to see that in this case  $V_{NN} \simeq V^{AB}$ , as expected.

With these parameters, as can be seen from Fig. 2, the nonlinearity is most pronounced at small values of  $l \leq 10$ . The chains of similar size were observed experimentally in Refs. [13, 14] for pure deposits. We expect that when alloyed with an appropriate second component (e. g., with copper in the case of gold) they can exhibit the same kind of narrowing the size distribution as was predicted by us for the self-assembly on the alloyed substrate [3]. Namely, assuming the optimum chain length dictated by the non-oscillating part of the Hamiltonian is seven (as in Refs. [10, 13]), the oscillating part will suppress the concentrations of the nearest chains of lengths 6 and 8 *in addition* to the usual suppression due to the Gaussian dependence of the distribution at low temperatures [9] dictated by the elastic and chemical parts.

#### 4. Conclusion

In this paper we discussed possible influence of alloying on the size distribution of atomic chains. Our solution of a simplified 1D model showed that if the atoms inside the chains tend to order at low temperatures, the size distribution became more narrowly peaked near the most probable chain length. This is similar to the case of the self-assembly of one-specie islands on alloyed substrates considered in Ref. [3]. The calculations show that the phenomenon is more pronounced at lower temperatures, in particular, it extends to longer optimum chain lengths. However, at low temperatures too long time may be needed to equilibrate the system. Therefore, it would be more reasonable to seek the confirmation of our theory in systems where the chains are very short, such as the Ag/Pt system studied in Refs. [10, 13] or the Au chains grown in Ref. [14]. Of course, it would be necessary to find the second component which under alloying would provide an

ordering alloy. In the bulk the copper would be a natural choice in the case of Au [see, e. g., 15, and references therein], but in 1D surface structures the interatomic interactions may significantly differ from those in 3D alloys [see discussion in 8].

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### Appendix A. Transfer matrix for binary alloy

The partition function for a strained chain composed of a binary alloy with components  $A$  and  $B$  of equal atomic diameters and pairwise nearest neighbor interatomic “chemical” interactions  $V_{i,j}^{\alpha\beta}$ , where  $\alpha, \beta = A, B$ , is (cf. [15, Ch. II])

$$\begin{aligned}
 Z_{\text{chain}}^{(l)} &= e^{-\bar{E}_i^{el}} \text{Tr} \exp \left( \sum_{\alpha=A,B} \sum_{i=1}^l \bar{\mu}_i^\alpha p_i^\alpha - \sum_{\alpha\beta=A,B} \sum_{i=1}^{l-1} p_{i+1}^\alpha \bar{V}_{i+1,i}^{\alpha\beta} p_i^\beta \right) \\
 &\equiv e^{-\bar{E}_i^{el}} \langle l | \hat{T}^{l-1} | 1 \rangle = e^{-\bar{E}_i^{el}} Z_{ch}^{(l)},
 \end{aligned} \tag{A1}$$

where the trace is taken over the occupation numbers  $\{p_i^\alpha\}$  which are equal to one if site  $i$  is occupied by atom of kind  $\alpha$  and are equal to zero otherwise. To simplify notation, we denoted by the bars the division by  $k_B T$ . For example,  $\bar{E}_i^{el} \equiv E_i^{el} / k_B T$ , where  $E_i^{el}$  is the elastic energy from Eq. (3). On the second line we introduced the



transfer matrix

$$\hat{T} = \begin{pmatrix} e^{\bar{\mu}^A - \bar{V}^{AA}} & e^{\bar{\mu}^A/2 - \bar{V}^{AB} \bar{\mu}^B/2} \\ e^{\bar{\mu}^A/2 - \bar{V}^{AB} \bar{\mu}^B/2} & e^{\bar{\mu}^B - \bar{V}^{BB}} \end{pmatrix} \equiv \begin{pmatrix} a & b \\ b & c \end{pmatrix}, \quad (\text{A2})$$

where

$$\langle l | = \left( e^{\bar{\mu}^A/2}, e^{\bar{\mu}^B/2} \right) \quad (\text{A3})$$

and  $|1\rangle = (\langle l |)^T$ . Furthermore, by the last equality in Eq. (A1) we separated the chain partition function into the elastic and the “chemical” parts.

To diagonalize the transfer matrix we need to solve the characteristic equation

$$\lambda^2 - \lambda(a + c) + ac - b^2 = 0, \quad (\text{A4})$$

$$\begin{aligned} \lambda_{\pm} &= \frac{a + c}{2} \pm \sqrt{\frac{(a + c)^2}{4} + b^2 - ac} \\ &= \frac{a + c}{2} \left( 1 \pm \sqrt{1 + R(e^{\bar{V}} - 1)} \right), \end{aligned} \quad (\text{A5})$$

where

$$R = \left( \frac{2}{\sqrt{a/c} + \sqrt{c/a}} \right)^2 \quad (\text{A6})$$

and

$$V \equiv V^{AA} + V^{BB} - 2V^{AB} \quad (\text{A7})$$

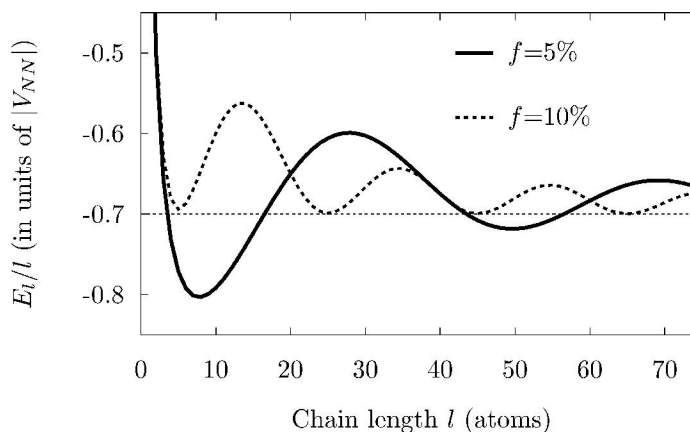
[see Eqs. (A2) and (A3)]. The orthogonal matrix  $\hat{O}$  which diagonalizes the transfer matrix

$$\hat{O}^T \hat{T} \hat{O} = \begin{pmatrix} \lambda_+ & 0 \\ 0 & \lambda_- \end{pmatrix} \quad (\text{A8})$$

is composed from normalized eigenvectors of  $\hat{T}$  (which can be easily found) as

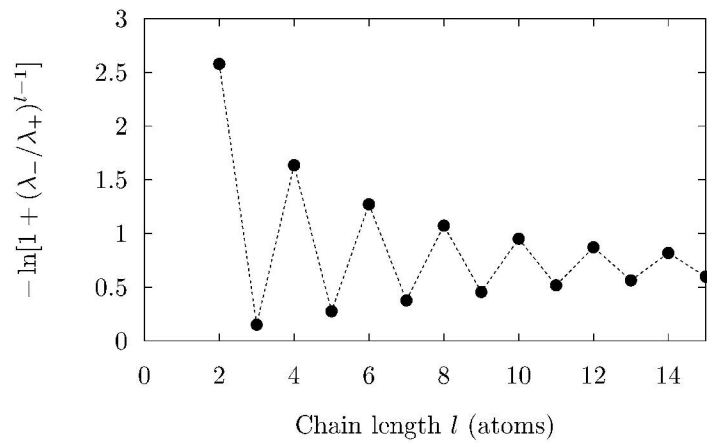
$$\hat{O} = \frac{1}{\sqrt{\lambda_+ - \lambda_-}} \begin{pmatrix} \frac{b}{\sqrt{|\lambda_+ - a|}} & \frac{b}{\sqrt{|\lambda_- - a|}} \\ \frac{b}{\sqrt{|\lambda_+ - a|}} & \frac{b}{\sqrt{|\lambda_- - a|}} \end{pmatrix} \quad (\text{A9})$$

$$\begin{aligned} Z_{ch}^{(l)} &= \frac{1}{\lambda_+ - \lambda_-} \left[ \left( \frac{be^{\bar{\mu}^A/2}}{\sqrt{|\lambda_+ - a|}} + e^{\bar{\mu}^B/2} \sqrt{|\lambda_+ - a|} \right)^2 \lambda_+^{l-1} \right. \\ &\quad \left. \left( \frac{be^{\bar{\mu}^A/2}}{\sqrt{|\lambda_- - a|}} + e^{\bar{\mu}^B/2} \sqrt{|\lambda_- - a|} \right)^2 \lambda_-^{l-1} \right]. \end{aligned} \quad (\text{A10})$$



**Reduced per atom energy of the chains of adsorbed atoms for two values of the misfit  $f$ . The substrate potential strength  $k$  in Eq. (\ref{V\_s}) was chosen to be equal to  $0.3|V_{NN}|$ . The horizontal line corresponds to the asymptotic value of  $E_i/l$  as  $l \rightarrow \infty$  [see Eq. (\ref{E\_i})]. The dashed curve which passes above this curve does not have a global minimum at finite  $l$ .**

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**Non-linear in  $l$  contribution to the effective interaction Eq. (\ref{dEch}) for alloyed chains of different length. For further explanations see the text**

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