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Exact solution of a one-dimensional model of strained epitaxy on a periodically modulated substrate

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We consider a one-dimensional lattice gas model of strained epitaxy with the elastic strain accounted for through a finite number of cluster interactions comprising contiguous atomic chains. Interactions of this type arise in the models of strained epitaxy based on the Frenkel-Kontorova model. Furthermore, the deposited atoms interact with the substrate via an arbitrary periodic potential of period L. This model is solved exactly with the use of an appropriately adopted technique developed recently in the theory of protein folding. The advantage of the proposed approach over the standard transfer-matrix method is that it reduces the problem to finding the largest eigenvalue of a matrix of size L instead of 2^{L-1}, which is vital in the case of nanostructures where L may measure in hundreds of interatomic distances. Our major conclusion is that the substrate modulation always facilitates the size calibration of self-assembled nanoparticles in one- and two-dimensional systems.

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I. INTRODUCTION

Periodic arrays of self-assembled nanostructures are expected to find important technological applications in such fields as optoelectronics, magnetic memory, and other microelectronic devices [1–3]. A natural way of producing such arrays is to perform growth on a substrate that is periodically modulated either due to some physical phenomenon, such as surface reconstruction [4], or by a direct lithographic patterning [5]. In particular, one- and quasi-one-dimensional (1D) chainlike arrays with cluster thickness of one or a few atoms are expected to bring the technology to the truly atomistic scale [6–13].

In this paper we consider an exactly solvable 1D model of strained epitaxy on a modulated substrate. The model is an extension of the previously solved model with a flat substrate [14,15] and is explained in the next section. The method of solution, however, is completely different. In this paper we will adopt the method proposed in Ref. [16] for finite systems in connection with the problem of protein folding. In Sec. III we present an alternative approach to this method appropriate to treat our model of strained epitaxy in the thermodynamic limit. The matrix equations arising in this limit are discussed in Sec. IV. The formulas for the cluster size distributions and other quantities of interest are derived in Sec. V. In Sec. VI we will show that the substrate modulation facilitates the size calibration of self-assembled clusters irrespective of the relative scales of the modulation and the size calibration. In conclusion we briefly discuss further possible applications and extensions of the results obtained.

II. THE MODEL

The model we are going to study is an extension of the lattice gas model introduced in our previous papers [14,15]. Its Hamiltonian

$$H = E_s + E_{\mathrm{chain}} \tag{1}$$

consists of two terms: the interaction with the substrate via a periodic potential v_i with period L_s

$$E_s = \sum_i v_i n_i, \tag{2}$$

where $n_i = 0, 1$ is the site occupation number, and an intrachain energy term which is given by a finite number of cluster interactions within contiguous atomic chains [14]

$$E_{\mathrm{chain}} = \sum_{i,l \leq L} V_l n_i n_{i+1} \cdots n_{i+(l-1)}. \tag{3}$$

Here L is the period of the system which we will define below; V_l are numerical coefficients connected with the energies of atomic chains of length l [14],

$$E_l = \sum_{j=1}^{l} (l + 1 - j) V_j, \tag{4}$$

as

$$V_l = E_l - 2E_{l-1} + E_{l-2}. \tag{5}$$

In Eq. (3) we included a translationally invariant term $V_1 \Sigma_i n_i$ which is similar to the substrate interaction term. So we assume that the mean value $\overline{v}$ of the substrate potential is absorbed into this term and in the following will consider substrate potentials that have zero mean value:

$$\sum_{i=1}^{L_s} v_i = 0. \tag{6}$$

Furthermore, we assume that the chemical potential is also included into V_1, so this term will be used to fix the number of particles in the system. The latter will be called the coverage because the model is supposed to describe epitaxy.

The values of the coefficients V_l calculated in the framework of the Frenkel-Kontorova model in Ref. [15] are exponentially small at large l, so the energies E_l can be fitted to any desired accuracy by a finite number of them. Therefore, we assume that their number $l_{\max}$ is finite and if it exceeds the period of the substrate potential L_s then we choose such an integer L which is a multiple of L_s that is greater than or equal to $l_{\max}$. This number will be called the period of the system.

Because the method of solution used by us is based on the chain energies, we introduce the energies of interaction of chains of length l with the substrate as [16]

$$w_l^N = \sum_{i=N+1-l}^{N} v_i. \tag{7}$$

We note that with the use of Eq. (6) it is easy to show that w_l^N is a periodic function of both l and N. In particular, from Eq. (6) it follows that

$$w_L^N = 0. \tag{8}$$

The physical meaning of w_l^N is the adsorption energy of the chain of length l whose end atom is placed at site N.

From Eq. (5) it follows that the internal chain energy E_l for $l \geqslant L$ is a linear function of l (the second derivative is zero):

$$E_l|_{l\geqslant L} = E_0 + E' l, \tag{9}$$

where

$$E_0 = \sum_{j=2}^{\infty} (1-j) V_j \tag{10}$$

and

$$E' = \sum_{l=1}^{\infty} V_l. \tag{11}$$

The last equation is obtained by the summation of Eq. (5) once; Eq. (10) is obtained as the difference between E_l and $E'l$ at large l. In the above equations we have set the upper limit of summation to infinity because all V_l are equal to zero for large l. This formal point will be useful when we calculate the distribution of chain sizes in Sec. VI.

III. METHOD OF SOLUTION

The above model can be solved with the use of the appropriately adopted method of Ref. [16]. Its advantage is that, as we will see below, the transfer matrix obtained is much smaller: of the size of the modulation period L instead of 2^{L-1} as in the standard approach. This is an important difference in the case of nanoscale objects when L may have values as large as hundreds of lattice spacings which makes the conventional technique useless.

In Ref. [16] the 1D model was solved by means of its mapping onto a 2D system. The derivation presented below is, in our opinion, somewhat simpler because it is based on purely 1D objects. This may allow for generalizations of the approach to more complex systems.

To be specific, we derive all equations for the model of the preceding section but the same derivation can be repeated for the general case considered in Ref. [16].

A few words about notation. To simplify the formulas below, some of which are rather cumbersome, in the following we will assume that all quantities of the dimension of energy are divided by the thermodynamic temperature $k_B T$. In case of necessity this temperature dependence can be restored from dimensionality considerations.

Thus, instead of the sequence of finite matrices introduced in Ref. [16] we consider an infinite matrix and the iterative scheme associated with it as

$$\begin{pmatrix} Z_0^{(N)} \\ Z_1^{(N)} \\ Z_2^{(N)} \\ Z_3^{(N)} \\ \vdots \\ Z_l^{(N)} \\ \vdots \end{pmatrix} = \left(\begin{array}{c|c|c|c|c|c|c} 1 & e^{-w_1^N - E_1} & e^{-w_2^N - E_2} & e^{-w_3^N - E_3} & \dots & e^{-w_l^N - E_l} & \dots \\ \hline 1 & 0 & 0 & 0 & \dots & 0 & \dots \\ \hline 0 & 1 & 0 & 0 & \dots & 0 & \dots \\ \hline 0 & 0 & 1 & 0 & \dots & 0 & \dots \\ \hline \vdots & \vdots & \ddots & \ddots & \ddots & \vdots & \vdots \\ \hline 0 & 0 & 0 & 0 & \ddots & 0 & \dots \\ \hline \vdots & \vdots & \vdots & \vdots & \ddots & \ddots & \ddots \end{array}\right) \begin{pmatrix} Z_0^{(N-1)} \\ Z_1^{(N-1)} \\ Z_2^{(N-1)} \\ Z_3^{(N-1)} \\ \vdots \\ Z_l^{(N-1)} \\ \vdots \end{pmatrix} \tag{12}$$

According to this scheme, the partition function $Z_0^{(N)}$ of the system consisting of N sites is obtained by N iterations of the above equation starting from the initial vector $Z_l^{(0)}$ with all components equal to zero except the first two:

$$Z_0^{(0)} = Z_1^{(0)} = 1. \tag{13}$$

As can be seen from Eq. (12), the only nontrivial matrix multiplication comes from the first line. The other lines simply serve to shift the components of $Z^{(N-1)}$ down by one position:

$$Z_l^{(N)} = Z_{l-1}^{(N-1)} = \cdots = Z_0^{(N-l)}, \quad N > l. \tag{14}$$

Thus, the nonzero components of $\mathbf{Z}^{(N)}$ are the partition functions for the numbers of sites $N, N-1, \ldots, 1$ and the above two "zero-site" terms $Z_N^{(N)} = Z_{N+1}^{(N)} = 1$. The proof of this statement can be carried out by induction. It will be sufficient to prove it only for the first component of $\mathbf{Z}^{(N)}$, i.e., $Z_0^{(N)}$, because other components are obtained from Eq. (14).

The case $N=1$ is easily checked directly. Let us assume that the above statement is valid for systems of all sizes smaller than N. Now we add the Nth site and consider all possible cases.

By adding an empty site we obtain just $Z_0^{(N-1)}$ multiplied by unity [the first term in the first row of the matrix in Eq. (12)]. Now if we want to add a site filled with an atom, there are the following cases possible. If the deposited atom turns out to be isolated, this would mean that the last site of the initial system consisting of $N-1$ sites was empty. Hence, its partition function was $Z_0^{(N-2)}$ multiplied by unity, as in the case just considered. So we have to additionally multiply it by the Boltzmann factor corresponding to an isolated atom (we recall that interatomic interactions exist only within contiguous chains). This factor is given by the second term in the first row of the matrix and is the negative exponential of the sum of the interaction with the substrate ($w_1^N = v_N$) and the contribution from our chemical potential $E_1 = V_1$.

Further terms correspond to the cases when the added atom becomes a member of the chain of length l:

$$\Delta Z_0^{(N)} = \underbrace{Z_0^{(N-l-1)}}_{N-l-1\ \text{sites}} \quad \underbrace{e^{-w_l^N - E_l}}_{l\text{-atomic chain}}\ , \tag{15}$$

where in counting the total number of sites one should add an empty site separating the $(N-l-1)$-site system from the l chain. The last two terms are given by the contributions from the system with $N-1$ atoms and a completely filled system with the factors Z given by Eq. (13).

The above iteration scheme can be applied to finite systems, but in this paper we consider in detail its application to the model of the preceding section in the thermodynamic limit $N\to\infty$. To this end we first assume that N is much larger then L and write down the expression for the partition function on the basis of Eq. (12) as

$$\begin{aligned} Z_0^{(N)} &= Z_0^{(N-1)} + \sum_{l=1}^{2L} e^{-w_l^N - E_l} Z_l^{(N-1)} + \sum_{l=2L+1}^{\infty} e^{-w_l^N - E_l} Z_{l-L}^{(N-L-1)} \\ &= Z_0^{(N-1)} + \sum_{l=1}^{2L} e^{-w_l^N - E_l} Z_l^{(N-1)} + e^{-E'L} \sum_{l=L+1}^{\infty} e^{-w_l^N - E_l} Z_l^{(N-L-1)}, \end{aligned} \tag{16}$$

where the second term in the first equality was transformed with the use of Eq. (14) and in the second equality the same term was further transformed by the change of the summation index from l to $l-L$. Furthermore, E_{l+L} was replaced by $E_l+E'L$ using Eq. (9) for $l\geqslant L$; because of the periodicity w_l^N is left unchanged.

The second term in the second line can be further transformed as

$$\sum_{l=1}^{2L} e^{-w_l^N - E_l} Z_l^{(N-1)} = \sum_{l=1}^{L} e^{-w_l^N - E_l} Z_l^{(N-1)} + e^{-E'L} \sum_{l=1}^{L} e^{-w_l^N - E_0 - E'l} Z_l^{(N-L-1)}. \tag{17}$$

Similarly, for the system of size $N-L$ Eq. (12) gives

$$Z_0^{(N-L)} = Z_0^{(N-L-1)} + \sum_{l=1}^{L} e^{-w_l^N - E_l} Z_l^{(N-L-1)} + \sum_{l=L+1}^{\infty} e^{-w_l^N - E_l} Z_l^{(N-L-1)}. \tag{18}$$

Now subtracting this equation multiplied by $\exp(-E'L)$ from the equation for Z_0^N we obtain a finite set of equations for the partition functions:

$$\begin{aligned} Z_0^{(N)} - Z_0^{(N-1)} = e^{-E'L}\left[Z_0^{(N-L)} - Z_0^{(N-L-1)}\right] + \sum_{l=1}^{L} e^{-w_l^N - E_l} Z_0^{(N-l-1)} \\ + e^{-E'L} \sum_{l=1}^{L-1} e^{-w_l^N} \left(e^{-E_0 - E'l} - e^{-E_l}\right) Z_0^{(N-L-l-1)}, \end{aligned} \tag{19}$$

where additionally use has been made of Eqs. (14) and (9). We note that this possibility to make the system of equations finite was due to the restriction of elastic forces by the finite number of interaction parameters V_l. Being put into a matrix form, this equation can be used as a finite-size version of the iterative scheme (12). It can be applied to finite systems with the finite extent of the cluster interactions. Its additional advantage over the conventional transfer matrix method (besides reducing the the matrix size) is that a system of any size is treated within the same formalism while in the former case one needs additional efforts to treat systems sizes that are not integer multiples of $L-1$ [28].

A. Thermodynamic limit

The number of unknown variables in the problem under consideration is formally equal to N. But because the system is periodic, in the thermodynamic limit $N\to\infty$ the influence of boundaries becomes unimportant and this number can be reduced to L. To do this we assume that asymptotically at large N the partition function behaves as

$$Z_0^{(N)}\big|_{N\to\infty} \sim \exp[-Nf + \phi_N + o(1)], \tag{20}$$

where f is the free energy per site and ϕ_N is of order unity and is periodic in N with period L. Equation (20) is a natural generalization of the expansion of the free energy at finite N in a series of the type $O(N^1)+O(N^0)+O(N^{-1})+\cdots$.

Substituting Eq. (20) into Eq. (19) we obtain an equation for $z=\exp(-f)$:

$$\begin{aligned} (e^{-E'L} z^{-L} - 1)(\psi_N - z^{-1}\psi_{N-1}) + \sum_{l=1}^{L} z^{-l-1} e^{-w_l^N - E_l} \psi_{N-l-1} \\ + e^{-E'L} z^{-L} \sum_{l=1}^{L-1} z^{-l-1} e^{-w_l^N} (e^{-E_0 - E'l} - e^{-E_l}) \psi_{N-l-1} = 0, \end{aligned} \tag{21}$$

where $\psi_i=\exp(\phi_i)$. Writing down the above equation for L different values of N and using the periodicity of ψ_i we can obtain a set of linear equations sufficient to find all distinct values of ψ_i. Because the set is homogeneous, it has nontrivial solutions only provided its determinant is equal to zero. The latter condition provides us with an equation to define z and hence the free energy per site f. But because the matrix in question is, in fact, a transfer matrix of a 2D model [16], only the largest eigenvalue is of interest. And finding the latter can be an easier task than the computation of the whole determinant, especially in the case of large L when the determinant—which is a homogeneous function of the matrix elements of order L—became difficult to compute with sufficient accuracy. Therefore, below we develop a formalism based on the largest eigenvalue approach.

IV. THE LARGEST EIGENVALUE APPROACH

The equations of the preceding section would allow us to find the grand canonical free energy of the system f as a function of our chemical potential V_1 and the temperature T included into the parameters of the system. With this solution one can use the standard grand canonical formalism to obtain all thermodynamic quantities of interest.

In the field of heteroepitaxal deposition at the surface, however, one is rarely interested in the thermodynamic quantities. This is partly because a surface with foreign atoms deposited on it is not thermodynamically stable (at equilibrium the deposited atoms should simply dissolve in the bulk) and partly because the thermodynamic quantities pertinent to the surface are not readily measured experimentally.

Instead, one is usually interested in such more easily observable quantities as the size distribution of self-assembled atomic clusters. Therefore, in this section we will develop a method of solution of the equations derived in the preceding section that is suitable for the calculation of such quantities. To this end we first remark that with the use of the parameter

$$x = z\exp(E') \tag{22}$$

Eq. (21) can be cast into the form

$$\psi_{N-1} + \sum_{l=1}^{L} x^{-l} e^{-w_l^N} d_l \psi_{N-l-1} = z\psi_N, \tag{23}$$

where

$$d_l = e^{E'l - E_l} + e^{-E_0}/(x^L - 1). \tag{24}$$

It is to be noted that the parameter x can be used as a replacement of our chemical potential variable V_1 because as is easily seen neither E_0 in Eq. (10) nor the combination $E'l - E_l$ depends on V_1, so Eq. (23) depends on V_1 only through the parameter x.

Thus, the set of equations (23) for L consecutive values of N can be written as a linear eigenvalue problem

$$\hat{M}\boldsymbol{\psi} = z\boldsymbol{\psi} \tag{25}$$

with matrix

$$\hat{M} = \left(\begin{array}{c|c|c|c|c|c}
\frac{d_{L-1}}{x^{L-1}}e^{-w_{L-1}^1} & \frac{d_{L-2}}{x^{L-2}}e^{-w_{L-2}^1} & \dots & \frac{d_2}{x^2}e^{-w_2^1} & \frac{d_1}{x}e^{-w_1^1} & 1+\frac{e^{-E_0}}{x^L-1} \\ \hline
1+\frac{e^{-E_0}}{x^L-1} & \frac{d_{L-1}}{x^{L-1}}e^{-w_{L-1}^2} & \dots & \frac{d_3}{x^3}e^{-w_3^2} & \frac{d_2}{x^2}e^{-w_2^2} & \frac{d_1}{x}e^{-w_1^2} \\ \hline
\frac{d_1}{x}e^{-w_1^3} & 1+\frac{e^{-E_0}}{x^L-1} & \dots & \frac{d_4}{x^4}e^{-w_4^3} & \frac{d_3}{x^3}e^{-w_3^3} & \frac{d_2}{x^2}e^{-w_2^3} \\ \hline
\vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ \hline
\frac{d_{L-3}}{x^{L-3}}e^{-w_{L-3}^{L-1}} & \frac{d_{L-4}}{x^{L-4}}e^{-w_{L-4}^{L-1}} & \dots & 1+\frac{e^{-E_0}}{x^L-1} & \frac{d_{L-1}}{x^{L-1}}e^{-w_{L-1}^{L-1}} & \frac{d_{L-2}}{x^{L-2}}e^{-w_{L-2}^{L-1}} \\ \hline
\frac{d_{L-2}}{x^{L-2}}e^{-w_{L-2}^L} & \frac{d_{L-3}}{x^{L-3}}e^{-w_{L-3}^L} & \dots & \frac{d_1}{x}e^{-w_1^L} & 1+\frac{e^{-E_0}}{x^L-1} & \frac{d_{L-1}}{x^{L-1}}e^{-w_{L-1}^L}
\end{array}\right) \tag{26}$$

where we used Eqs. (8) and (9) to simplify the matrix elements corresponding to $l=L$.

As we see, the eigenvalue problem (25) is not symmetric. But from Eq. (23) we can conclude that x should be larger then unity, at least for a system of equations that is consistent for all allowed values of the system period. The latter can be chosen as an arbitrarily large integer multiple of L so the summation in Eq. (23) should be convergent. But this is possible only for $x>1$ because at large l all other factors under the summation sign either oscillate (ψ_i) or saturate to constant values, as can be seen from the expressions for d_l [Eq. (24)] and the quantities entering it.

If $x>1$ then the matrix $\hat{M}$ is strictly positive and according to the Perron-Frobenius theorem (see the Corollary to Theorem 9.2.2 in Ref. [18]) it has a real positive nondegenerate eigenvalue with its value exceeding the moduli of all other eigenvalues. The right eigenvector associated with it (our vector $\boldsymbol{\psi}$) is also positive. It is this eigenvalue and eigenvector that we associate with the physical solution of the eigenvalue problem (25).

The eigenvalue problem can be treated in two ways. We can use the grand canonical formalism by fixing V_1 and solving the characteristic equation

$$\det(\hat{M} - z\hat{I}) = 0 \tag{27}$$

with x given by Eq. (22). An alternative way would be to consider Eq. (25) as a linear eigenvalue problem. In this case x is considered as a thermodynamic variable which implicitly defines V_1 through Eq. (22).

A. Ising model in staggered field

To illustrate the first of the above approaches we consider a simple problem where the exact solutions can be obtained independently by the conventional transfer-matrix method. This solution is presented in the Appendix.

As is known, the Ising model is equivalent to the lattice gas model [17], so the Ising model in the staggered magnetic field would correspond to a system of the type considered in the present paper with all V_l equal to zero except the nearest neighbor interaction V_2 and the variable V_1. The substrate potential would be a binary-alloy-type potential with two values $\pm v$ on alternating sites. Thus, the model is periodic with period $L=2$ and the matrix in Eq. (26) with $E_0=-V_2$, $E'=V_1+V_2\equiv H$, and $E'l-E_l|_{l=1}=V_2$ is

$$\hat{M} = \frac{1}{x^2-1}\begin{pmatrix} xe^{V_2-v} & x^2-1+e^{V_2} \\ x^2-1+e^{V_2} & xe^{V_2+v} \end{pmatrix}. \tag{28}$$

Being substituted into Eq. (27), this matrix leads to a characteristic equation of the sixth order in z. Because such an equation cannot be straightforwardly solved analytically, we checked it numerically. By substituting λ_+ from Eq. (A5) into Eq. (27) with x given by Eq. (22) we found that the characteristic equation is satisfied to within the accuracy of the computation.

V. CALCULATION OF OBSERVABLE QUANTITIES

As was mentioned in the preceding section, of major interest in epitaxial studies are those quantities which can be directly observed via microscopy techniques. As we will see, the parametrization of matrix $\hat{M}$ with the variable x and the linearization of the eigenvalue equation connected to it provides us with a convenient formalism for the calculation of such quantities.

In contrast to V_1 which is linearly related with the chemical potential μ ($V_1=-\mu+\text{const}$), the variable x is connected to other quantities through the nonlinear Eq. (22). Thus, the change of variables from V_1 to x is, in fact, an introduction into the problem of curvilinear coordinates, so care must be taken in calculating the physical quantities of interest which are usually expressed as derivatives of f with respect to some parameters.

Let α be such a parameter and the quantity of interest is $\partial f/\partial\alpha$. With the solution of Eq. (25) given as the function of the parameter x and α which we will denote simply as z,

$$z = z(x,\alpha) = \exp(-f), \tag{29}$$

and taking into account that the variables are connected through Eq. (22) we have

$$\frac{df}{d\alpha} = -\frac{1}{z}\frac{\partial z}{\partial\alpha} - \frac{x}{z}\frac{\partial z}{\partial x}\left(\frac{dE'}{d\alpha} - \frac{df}{d\alpha}\right). \tag{30}$$

In the case of the variable $\alpha = V_1$ which is conjugate to the coverage $\theta = df/dV_1$, one finds

$$\theta = \left[1 - \left(x\frac{\partial \ln z}{\partial x}\right)^{-1}\right]^{-1}, \tag{31}$$

where use has been made of Eq. (11). This allows us to rewrite Eq. (30) as

$$\frac{df}{d\alpha} = -\frac{1-\theta}{z}\frac{\partial z}{\partial\alpha} + \theta\frac{dE'}{d\alpha}. \tag{32}$$

In the systems exhibiting the phenomenon of self-assembly one is usually interested in the size distribution of the atomic clusters. The concentration c_k of clusters of size k can be calculated as the statistical average of the product [16]

$$\begin{aligned} m_k &= (1-n_i)n_i n_{i+1}\cdots n_{i+k}(1-n_{i+k+1}) \\ &= \prod_{j=1}^{k} n_{i+j} - 2\prod_{j=1}^{k+1} n_{i+j} + \prod_{j=1}^{k+2} n_{i+j}, \end{aligned} \tag{33}$$

where in the last equality we assumed translation invariance in the thermodynamic limit. From this equality and from Eqs. (1) and (3) it is seen that the average value of m_k can be calculated as

$$c_k \equiv \langle m_k\rangle = \left(\frac{\partial}{\partial V_k} - 2\frac{\partial}{\partial V_{k+1}} + \frac{\partial}{\partial V_{k+2}}\right) f \equiv \mathcal{D}_k f. \tag{34}$$

In the calculations of the cluster concentrations in the model under consideration the following relations will be useful:

$$\mathcal{D}_k E' = \mathcal{D}_k E_0 = 0 \tag{35}$$

and

$$\mathcal{D}_k E_l = \delta_{kl}. \tag{36}$$

A. Strained epitaxy on a flat substrate

Our second illustrative example is the model of Ref. [14] where the size calibration on the substrate corresponding to $v_i = 0$ in our present model was solved.

Because the substrate potential is fully translationally invariant, i.e., $L_s = 1$, the parameter L is defined by the extent of the interactions V_l. But irrespective of the value of L it is easy to see that matrix $\hat{M}$ becomes a circulant matrix so its maximum eigenvalue can immediately be written down explicitly as the sum of the matrix elements in one row [18],

$$z = 1 + \sum_{l=1}^{\infty} x^{-l} e^{E'l - E_l}, \tag{37}$$

where we assumed that interactions extend to infinity and used the assumption that $x > 1$.

Now using Eqs. (32), (35), and (36) one obtains

$$c_k = \frac{1-\theta}{z} x^{-k} e^{E'k - E_k}. \tag{38}$$

The total number of clusters (an observable quantity)

$$c = \frac{1-\theta}{z}\sum_{l} x^{-l} e^{E'l - E_l} \tag{39}$$

can be used to express z in Eq. (37) through observable quantities as

$$z = (1-\theta-c)/(1-\theta). \tag{40}$$

This expression when substituted in Eq. (38) would give us the solution in the form obtained in Refs. [14,15] by an independent method.

B. Calculation of derivatives

The derivatives of z with respect to the parameters that are necessary to calculate the physical quantities of interest according to the formulas derived above can be performed in various ways. The straightforward numerical differentiation would require solving the matrix equation for very close values of parameters which might be difficult to do with sufficient accuracy in the case of large L. An alternative way would be to use the characteristic equation (27) and to use formulas for the differentiation of the implicitly defined function $z(x,\alpha)$ and the formulas for the derivatives of determinants [18].

We found the following approach to be most practical. First, in addition to the eigenvalue one has to find also corresponding left and right eigenvectors of Eq. (25). We will denote them as $\bar{\boldsymbol{\psi}}$ and $\boldsymbol{\psi}$, respectively, and normalize as

$$\bar{\boldsymbol{\psi}}\cdot\boldsymbol{\psi} = 1. \tag{41}$$

The derivative in Eq. (32) is then calculated with the use of the Hellmann-Feynman theorem as

$$z'_\alpha = \bar{\boldsymbol{\psi}} M'_\alpha \boldsymbol{\psi}. \tag{42}$$

This formula can also be used to compute the derivative with respect to x to find the coverage θ in Eq. (31). The advantage of such an approach is most clearly seen when the cluster size distribution is calculated. As is seen from Eqs. (36) and (26), the derivative $\mathcal{D}_k$ of matrix $\hat{M}$ is a matrix with only nonzero matrix elements

$$(\mathcal{D}_k\hat{M})_{k+l \bmod L,\, l-k-1 \bmod L} = x^{-k} e^{E'k - E_k}\exp(-w_k^{l-k-1}), \tag{43}$$

where $l = 1, \ldots, L$. The modulo of a number m is defined as the positive number from 1 to L. The structure of this matrix is such that the corresponding average in Eq. (42) can be written as

$$z'_k = x^{-k} e^{E'k - E_k} \sum_{l=1}^{L} \overline{\psi_l} \exp(-w_k^l) \psi_{l-k-1 \bmod L}$$
$$= x^{-k} e^{E'k - E_k} \overline{\boldsymbol{\psi}} \cdot e^{-\mathbf{w}_k} \boldsymbol{\psi}(\circlearrowright L - k - 1), \quad (44)$$

where in the second equality we symbolically denoted the componentwise multiplication by a kind of a dot product whose definition should be understood from the first line and by the arrowed circle we denoted the circular shift of the right vector by $L-k-1$, which is equivalent to the modular arithmetic used by us.

The advantage of the last formula is that it is valid, as is easily seen, for arbitrary values of k. Indeed, according to our method of solution, if we would like to compute the size distribution for $k>L$ then we ought to enlarge the matrix $\hat{M}$ m times so that mL is greater then k. Then we should add the interactions V_k, V_{k+1}, and V_{k+2} and to compute the derivatives in Eq. (34). This could have been done either explicitly or implicitly via the characteristic equation. In both calculations the above values of V_i should be set to zero at the end of the calculation because they were necessary only as source terms to compute the derivatives. But this means that the true period of the system is still L and the function $\boldsymbol{\psi}$ of the enlarged system is the same as in the smaller system, only considered on m periods instead of one. As is easily seen, because of the periodicity of both $\boldsymbol{\psi}$ and w_l^N, the cyclic product in the second line of Eq. (44) will have the same value irrespective of whether it is calculated with the extended function or with the one corresponding to the minimal period L. It is this simplicity of going beyond the system period L for the size distribution which makes the approach based on the largest eigenvalue more convenient than other approaches mentioned above.

VI. CLUSTER SIZE DISTRIBUTION WITH MODULATED SUBSTRATE

It is quite obvious that if the potential of a modulated substrate is of sufficiently large amplitude, then the atomic distribution will follow the modulation with atoms gathering into clusters in the regions with the largest negative potential values. Thus, well separated and sufficiently deep potential wells will provide a necessary arrangement of the cluster array.

Less trivial is the observation that we are going to substantiate below that the substrate potential and the interatomic forces interfere in such a way that the size calibration of self-assembled clusters is *always* facilitated by the modulation, even in the cases when the period of modulation is much smaller then the cluster size.

To show this, let us first consider the condition of the size calibration in the absence of the substrate. In this case it reduces to the existence of a minimum in the per atom energy curve E_l/l [19]. The existence of a minimum means that the above dependence exhibits asymptotic growth at large l [15]. In our notation this would mean that E_0 is negative:

$$\left.\frac{E_l}{l}\right|_{l\to\infty} \sim \frac{E_0}{l} + E'. \quad (45)$$

Obviously a constant substrate potential $\overline{v}$ does not influence the self-assembly, which formally follows from the fact that its interaction with the atomic cluster is $\overline{v}l$ so its contribution into the above reduced energy curve is an l-independent constant.

Let us consider a potential well of depth $v_w<0$ and width w. At large distances from the well its contribution into the reduced energy will be growing as $v_w w/l$, i.e., quite expectedly it will facilitate the self-assembly. If we consider a periodic array of such wells, then the contribution into the assembly condition will take a more complicated form because this time the cluster can experience the periodic potential. So the curve will have many local minima positioned near the well minima, so the condition (45) will change to

$$\left.\frac{E_l}{l}\right|_{l\to\infty} \sim \frac{E_0}{l} + E' + \frac{w_l^l}{l} + \overline{v}, \quad (46)$$

where w_l^l is the periodic function defined in Eq. (7). Thus, in order for a global minimum to exist the local minima of this curve corresponding to the distant wells should grow with distance. It is easy to see that this condition can be written as

$$E_0 + \min(w_l^N) < 0. \quad (47)$$

An interesting property of this expression is that it does not include information about the interwell distance. Thus, we may conclude that the substrate aided size calibration will take place even if the self-assembled clusters extend over many wells.

To check this conclusion let us consider the extreme case of the binary-alloy-like potential as in Sec. IV A with $v_i = \pm v$ and let us assume that E_0 is positive, i.e., there is no size calibration on a flat substrate. For definiteness let us consider the chain energies as derived in Ref. [20] from the Frenkel-Kontorova model:

$$E_l = V_{\rm NN}(l-1) + A f_m^2 \frac{(l-1)^2}{2\Lambda}[1 - e^{-2\Lambda/(l-1)}], \quad (48)$$

where $V_{\rm NN}$ is the attractive nearest neighbor interaction, A is an elastic constant, f_m is the relative misfit between the substrate and the deposit, and $\Lambda = 3\pi/2$ is the relaxation length.

In the calculations below the strength of the elastic interaction was $Af_m^2 = 0.15|V_{\rm NN}|$. In this case the value of E_0 calculated according to Eq. (10) was approximately $0.35|V_{\rm NN}|$, i.e., positive and quite large in comparison with $V_{\rm NN}$. Thus, according to Eq. (47) the critical value of v above which the size calibration should be expected is $v_c = 0.35|V_{\rm NN}|$. In Fig. 1 the size distributions of the self-assembled clusters at different values of the substrate potential are shown. As can be seen, the distributions are indeed strongly peaked for the values of the substrate potential exceeding this value. The difference between the distributions with the substrate potential amplitude below and above the critical value is illustrated in Fig. 2. One can see that on lowering the temperature

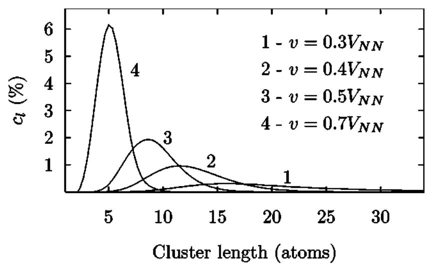

FIG. 1. Size distribution of self-assembled clusters at the inverse temperature $\beta = |V_{\mathrm{NN}}|/kT = 50$ and coverage $\theta = 0.5$ for different values of the substrate binary-alloy-like potential $\pm v$. The points corresponding to odd values of l are connected by lines for better visualization. The cluster concentrations corresponding to even l are at least seven orders of magnitude smaller then their neighbors corresponding to odd values.

in the case $v > v_c$ the atoms strive to gather into size calibrated clusters while in the case $v < v_c$ they tend to gather into a single large cluster.

VII. CONCLUSION

In this paper we considered a one-dimensional model of strained epitaxy on a modulated substrate. Besides being an exactly solvable model system to study some general questions of self-assembly on modulated substrates, this model can also serve to interpret experimental data on real one- or quasi-one-dimensional systems like those studied, e.g., in the papers cited in the Introduction or in Refs. [6,21–24]. Such an application is facilitated by the fact that the model is sufficiently general by admitting an arbitrary substrate potential and an infinite number of cluster interactions of arbitrary strength. Of course, the restriction to chain interactions is rather severe but it may be hoped that the method of solution proposed in Sec. III can be extended to more general models. This is supported by the fact that in Refs. [14,15] we were able to exactly solve the model on a flat substrate with additional next nearest neighbor interactions present.

An additional advantage of our solution with respect to the canonical transfer-matrix method besides reducing the dimension of the matrix from 2^{L-1} to L is that the solution obtained has a relatively simple analytical structure. This can be important if the model is used to fit experimental data on the size distributions to retrieve the values of the interaction parameters. At present they cannot be reliably calculated *ab initio* so the calculations are frequently supplemented by a fit to empirical potentials and to the Frenkel-Kontorova model [25–27].

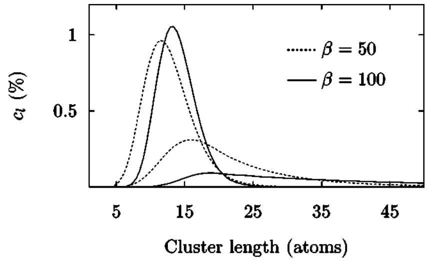

FIG. 2. Size distributions for two different values of the periodic substrate potential: one value $v = 0.3|V_{\mathrm{NN}}|$ lower than $v_c \approx 0.35|V_{\mathrm{NN}}|$ and the other value greater than v_c, where v_c is the critical value for the size calibration. The lines are drawn in the same way as in Fig. 1. It is seen that on lowering the temperature the size distribution of calibrated clusters becomes taller and narrower while the distribution for $v < v_c$ broadens and tends to zero.

The technique developed in the present paper can also be used to study finite systems. Here an additional advantage is that our formalism remains the same for the system consisting of any number of sites N while in the conventional transfer-matrix approach only the systems with N proportional to $L-1$ can be treated with the same ease [28] while in the case of N incommensurate with $L-1$ additional efforts are needed to account for boundary sites.

Finally, the conclusion that the modulated substrate always facilitate the size calibration was based on the existence of a global minimum in the reduced energy and is not connected to the specific model used. Therefore, this conclusion should be valid also in the case of 2D self-assembly because both the chemical and the elastic forces act independently along two orthogonal directions, so the reasoning of the previous section which led us to the size calibration criterion is valid for each direction [20,29]. Thus, we conclude that by periodically modulating the surface potential in two orthogonal directions would always facilitate the self-assembly of size calibrated clusters.

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APPENDIX: ISING MODEL IN STAGGERED FIELD

In order to facilitate comparison with the model of the main text we use the formalism of the lattice gas model to which the Ising model is equivalent (see, e.g., Ref. [17]).

With the nearest neighbor interatomic interaction denoted V_2 and the substrate potential taking the values V_1+v and V_1-v on alternating sites the partition function can be written as

$$Z = \sum_{n_1=0,1} \cdots \sum_{n_N=0,1} \prod_i \exp\left(-V_2 n_i n_{i+1} - \frac{1}{2}(v_i n_i + v_{i+1} n_{i+1})\right). \tag{A1}$$

This can be written as a product of 2×2 matrices

$$\hat{t}_i = \begin{pmatrix} 1 & e^{-(V_1 \pm v)/2} \\ e^{-(V_1 \mp v)/2} & e^{-H} \end{pmatrix}, \tag{A2}$$

where $H = V_1 + V_2$.

In order to represent Z as a power of a transfer matrix we should multiply matrices (A2) on two neighboring sites because the elementary cell of the system contains two sites:

$$\hat{t}_i\hat{t}_{i+1} = \begin{pmatrix} 1 + e^{-V_1-v} & e^{-(V_1-v)/2} + e^{-(V_1+v)/2-H} \\ e^{-(V_1-v)/2} + e^{-(V_1+v)/2-H} & e^{-V_1+v} + e^{-2H} \end{pmatrix}. \tag{A3}$$

The largest eigenvalue of this matrix is

$$\lambda_+^2 = e^{-H}[\cosh H + e^{V_2}\cosh v + \sqrt{(\cosh H + e^{V_2}\cosh v)^2 - (1-e^{V_2})^2}]. \tag{A4}$$

We denoted this eigenvalue as the square of λ_+ because it corresponds to two sites. The quantity to be compared with the partition function per site z in Sec. IV A is

$$\lambda_+ = e^{-H/2}[\sqrt{\cosh^2(H/2) + e^{V_2}\sinh^2(v/2)} + \sqrt{\sinh^2(H/2) + e^{V_2}\cosh^2(v/2)}]. \tag{A5}$$

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