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Scaling in the equilibrium size distribution of one-dimensional surface clusters

V. I. Tokar[1,2] and H. Dreyssé[1]
[1]*IPCMS-GEMM, UMR 7504 CNRS, 23 rue du Loess, F-67034 Strasbourg Cedex, France*
[2]*Institute of Magnetism, National Academy of Sciences, 36-b Vernadsky str., 03142 Kiev-142, Ukraine*
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The length distribution of the one-dimensional atomic rows self-assembled on a crystal surface in thermal equilibrium at low coverage is calculated both in the framework of an analytical theory and with the use of the Monte Carlo simulations. It has been shown that in the case of interatomic interactions restricted to nearest-neighbor atoms the distribution exhibits the scaling properties formally similar to those found in the theories of irreversible growth. The difference consisted in the behavior of the scaling functions which in the equilibrium case was monotonously decreasing while in the case of irreversible growth exhibits a monomodal character. We found that our scaled distribution described without any fitting parameters the monotonous distributions recently observed in the growth of Ga rows on Si(001) by Albao *et al.* [Phys. Rev. B **72**, 035426 (2005)]. The implications of the scaling for the experimental definition of interatomic interaction parameters is briefly discussed.

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I. INTRODUCTION

The processes of the self-assembly of the atomic clusters from the atoms deposited on a crystal surface at low temperature is currently the subject of intense study because such processes govern the growth of technologically important surface nanostructures.[1] The main difficulties in understanding and modeling such processes stem from the large number of parameters governing their behavior. For example, the adequate description of the equilibrium interactions between only two adatoms requires dozens of the pair free energies corresponding to different interatomic distances to be known.[2] Besides, the contribution of the many-atom interactions into the cluster energy can be comparable to the pair contributions[2] while the possible number of cluster types is a combinatorial quantity which can reach very large values. Furthermore, the kinetic parameters, such as anisotropic energy barriers essentially augment the number of parameters necessary for a predictive simulation of the nanostructure growth. Because of the above and because the gathering of the island statistics is a complicated and time consuming procedure, it is often difficult to gather enough data to differentiate between possible models describing the experiment.[3]

Therefore of particular importance for the growth studies are the cases when the number of the parameters is diminished in comparison with the general case so that their values can be reliably derived from available data. Such reduced description may be possible, for example, due to the simplicity of the cluster geometry, as in the case of one-dimensional (1D) clusters (see Refs. 2–4 and references therein).

Another possibility is the simplification of the kinetics at low temperature caused by the irreversibility of the atomic attachment to the clusters.[5] In this case the growing islands can sometimes (for instance, at low coverage smaller than ~10%) be modeled by sizeless point sinks where the diffusing atoms disappear irrespective of the strength and character of the interatomic interactions. This behavior can be described by universal island size distributions characterized by only a few parameters.[5–7] And because the scaling function is universal, i.e., independent of the individual details of the system studied, all cluster data are used to fit to those few parameters—thus essentially improving the accuracy of their determination.

In view of the above it seems logical to assume that the processes of growth of 1D clusters at low temperature would be especially amenable to quantitative model description. Experiments of Ref. 3 on the growth of 1D Ga rows on the Si(100), however, showed that in this and in several other cases the scaled size distribution of the clusters do not exhibit the expected monomodal character[5] but shows instead a monotonous dependence on the island size. Such a behavior was explained by a special relation between the diffusion parameters describing the anisotropy of the atomic diffusion in the system.

The aim of the present paper is to point out that the size distributions of the above type appear naturally at the equilibrium in the model with nearest-neighbor interatomic interaction. Moreover, the equilibrium size distributions exhibit the scaling behavior and describe the observed scaled cluster size distributions without any fitting. While the interatomic interaction derived from the experimental data seems to be too small in comparison with the *ab initio* calculations for the Ga/Si(100) system,[8] we argue that the proposed approach may turn out to be useful in other systems exhibiting the growth via the formation of 1D clusters.

In the next section we will derive an approximate analytical theory of the equilibrium size distributions of 1D clusters in the framework of the approach of Ref. 9. In the third section this theory will be verified with the Monte Carlo (MC) simulation of a lattice gas model with strongly anisotropic interatomic interactions. In the last section some implications of the results obtained will be discussed.

II. EQUILIBRIUM STATISTICS OF ONE-DIMENSIONAL CLUSTERS

Our analytical approach will be based on the formula for the size distribution of two-dimensional (2D) surface clusters derived by Priester and Lannoo[9] with the use of the mass-action law as

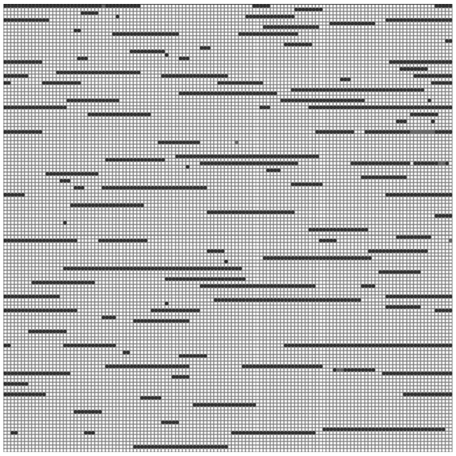

FIG. 1. Typical configuration of atoms on the surface obtained at the end of the MC simulation described in the text. The dark circles are the deposited atoms, the white squares are the deposition sites at the surface.

$$N_s = \exp\left[\frac{\mu s - E(s)}{kT}\right], \tag{1}$$

where N_s is the density per site of the clusters consisting of s atoms, $E(s)$ the energy of such clusters, and the parameter μ is similar to the chemical potential in that it can be used to fix the number of the deposited atoms.

To justify the applicability of this formula to the 1D clusters we first invoke the rigorous results of Refs. 10 and 11 where for a class of 1D models we have shown that Eq. (1) is exact up to the excluded-volume factor $1-\theta-N_{isl}$, where $N_{isl}=\Sigma_s N_s$ is the total density of islands. This factor can be approximately replaced by unity because the scaling in the size distributions during the epitaxial deposition is restricted to coverages lower then $\sim 10\%$ in the case of the anisotropic diffusion.[5] Besides, it is easy to see that N_{isl} is connected with θ through the average island size $\langle s\rangle$ as

$$N_{isl} = \theta/\langle s\rangle. \tag{2}$$

Because $\langle s\rangle$ is always no less than unity, N_{isl} is small whenever the coverage is small. From here it follows that, on the one hand, our theory of scaling at equilibrium is valid only at low coverages but, on the other hand, its accuracy is similar to that of the conventional theories of the scaling during irreversible growth.[5]

In the case of extremely anisotropic interactions considered in the present paper, the atoms gather into 1D islands or chains of atoms similar to those shown in Fig. 1.

In the simplest approximation of only nearest-neighbor (NN) interatomic interactions the energy of the chain consisting of s atoms is

$$E(s) = V_{NN}^x(s-1), \tag{3}$$

where V_{NN}^x is the attractive NN interatomic interaction in the binding direction which was chosen to be along the x axis. With the above island energy their size distribution according to Eq. (1) became exponential,

$$N_s = \exp\left(\frac{V_{NN}^x}{kT}\right)\exp\left[(\mu - V_{NN}^x)s/kT\right], \tag{4}$$

so that the total density of islands (which is an observable quantity) can be calculated as the sum of the geometric series as

$$N_{isl} = \sum_{s=1}^{\infty} N_s = \frac{1}{\exp(-\mu/kT) - \exp(-V_{NN}^x/kT)}. \tag{5}$$

As was mentioned earlier, the value of μ can be fixed from the known value of the coverage

$$\theta = \sum_{s=1}^{\infty} sN_s = \frac{\exp(-\mu/kT)}{[\exp(-\mu/kT) - \exp(-V_{NN}^x/kT)]^2}. \tag{6}$$

The latter formula can be obtained by differentiating Eq. (5) with respect to μ/kT, as is easy to see from the formula (4) for N_s.

Because in the experiments on the cluster size distributions the interatomic interaction V_{NN}^x is not known, we exclude it from the consideration with the use of the above equations. From definition (2) of the average island size and Eqs. (6) and (5) it follows that

$$\exp(\mu/kT) = \theta/\langle s\rangle^2. \tag{7}$$

Substituting this into Eq. (5) and using the definition of the average island size (2) one obtains

$$\exp(-V_{NN}^x/kT) = \langle s\rangle(\langle s\rangle - 1)/\theta. \tag{8}$$

Substitution of Eqs. (7) and (8) into Eq. (1) gives

$$N_s = \frac{\theta}{\langle s\rangle^2}\frac{[(1-1/\langle s\rangle)^{\langle s\rangle}]^{s/\langle s\rangle}}{(1-1/\langle s\rangle)}. \tag{9}$$

When the average island size is sufficiently large the variable $x=s/\langle s\rangle$ may be approximately considered to be continuous variable with $dx \approx 1/\langle s\rangle$. In this case Eq. (9) can be cast into the canonical scaling form[5]

$$N_s = \frac{\theta}{\langle s\rangle^2}f(x), \tag{10}$$

where in our case the scaling function is just the negative exponential of x

$$f(x) = \exp(-x) \tag{11}$$

which trivially satisfies the sum rules following from Eqs. (6) and (5):

$$\int_0^{\infty} f(x)dx = \int_0^{\infty} xf(x)dx = 1 \tag{12}$$

which coincide with corresponding normalizations of Ref. 3 presented after Eq. (1) of that reference. In Fig. 2 we compare the experimental data on the scaled distributions[3] with the above expressions. It is remarkable that contrary to the theory of Ref. 3 we do not need any fitting parameters to obtain the agreement similar to that obtained in the above reference.

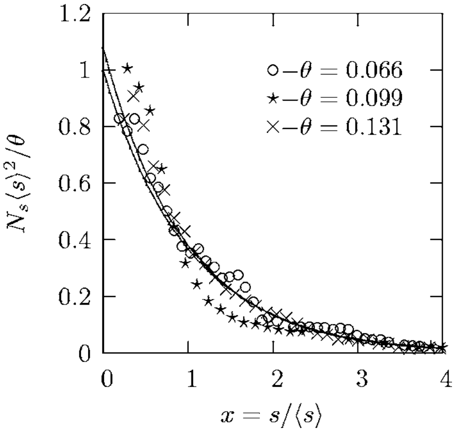

FIG. 2. Finite-size [upper solid line, Eq. (9)] and asymptotic $\langle s\rangle \to \infty$ [lower solid line, Eqs. (10) and (11)] theoretical scaled island size distributions compared with the experimental data from Ref. 3; for simplicity only the lowest, the medium, and the largest coverages from those studied in the above reference are shown.

Solving Eq. (8) with respect to $\langle s\rangle$ allows one to obtain an explicit expression for the coverage dependence of the average island size as

$$\langle s\rangle = 0.5[1 + \sqrt{1 + 4\theta \exp(-V_{NN}^x/kT)}]. \tag{13}$$

Because the absolute value of the interatomic interaction $|V_{NN}^x|$ at typical experimental temperatures is much larger then kT, the exponential in the right-hand side of this equation is usually very large, so to a good accuracy the above expression can be approximated as

$$\langle s\rangle \approx \sqrt{\theta} \exp(-V_{NN}^x/2kT). \tag{14}$$

In this case we need to fit the interaction parameter to obtain the agreement with the experimental data (see Fig. 3). Comparison between the fitted value of the pair interaction V_{NN}^x and those obtained for the interatomic binding of group-III metals on the Si(001) surface in *ab initio* calculations[8,12] will be made in Sec. IV of this paper.

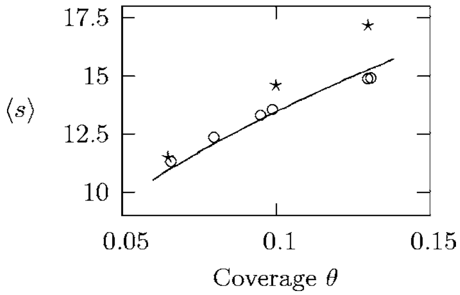

FIG. 3. The dependence of the average island size on coverage given by Eq. (13) (solid line) fitted to the experimental values of $\langle s\rangle$ derived from the data of Ref. 3 (circles). With the room temperature ~300 K the pair interaction was found to be $V_{NN}^x \approx -0.192$ eV. The stars show the values obtained in the numerical simulations described in the text.

III. MONTE CARLO SIMULATION

In the previous section we introduced a lattice gas model for the description of the equilibrium distribution of the sizes of the 1D islands. Because the analytical theory used was originally proposed for 2D islands, one may wonder whether the approximations developed in Ref. 9 are appropriate in the 1D case.

To check this, Monte Carlo simulations were performed with the use of the standard activated dynamics.[13] The latter requires that the activation energies to be known for any atomic configuration. The latter were calculated according to the conventional rules.[13] The bond energy was chosen to be equal to the above fitted value (see Fig. 3). The blocking of sites on the sides of the chains introduced in Ref. 3 was achieved by assuming that the nearest-neighbor interatomic interaction is anisotropic with $V_{NN}^x = -0.192$ eV and $V_{NN}^y = 0.1$ eV. The latter value was chosen in accordance with Ref. 12 where the chains of another group-III metal (Al) were studied. The exact value of V_{NN}^y was not very important because of the low temperature $T = 300$ K ≈ 0.026 eV, so that the probability of finding an atom on a NN site of an island in the y direction is strongly suppressed for all positive values of V_{NN}^y which essentially exceed the above value of T. The origin of the interatomic repulsion will be discussed in Sec. IV.

Our statistical approach is based on the assumption that the flux of deposited atoms is so small with respect to the mobility of the atoms on the surface that the system is in the state thermal equilibrium. Because the state of equilibrium does not depend on the kinetic path leading to it, we did not simulate the process of the atomic deposition in order to avoid using the same kinetic path as that used in Ref. 3 (otherwise it would be impossible to state that our results are a consequence of the equilibrium statistics and not the kinetics, as in Ref. 3). Instead, the number of atoms corresponding to the coverage under consideration was randomly placed on the surface and then annealed until the equilibrium was reached. For the same reason of independence of the state of equilibrium from the kinetics leading to it, simple isotropic atomic hopping dynamics were used in the simulations. The substrate lattice was modeled by a square with the side $L = 128$ lattice units and periodic boundary conditions. This size of the simulated system is comparable to the size in 100 lattice units used in the MC study of the island size scaling in Ref. 14. Also, the ratio of the average side length of 2D square islands $l_{2D} = \sqrt{\langle s\rangle}$ to the system size is similar to that of Ref. 15. In the latter reference the island size reached $l_{2D} \approx 20$ with $L = 200$ while in our case the average island length l_{1D} was in the range 11–17 (see Fig. 3) and $L = 128$.

The event-based algorithm of Ref. 16 was used to speed up the simulation at low temperature where the acceptance rate in the conventional Metropolis algorithm is small.[17] The time of the evolution was measured in the units of inverse hopping rate (IHRU) of a free atom. The annealing was performed during $t_{tot} = 5 \times 10^5$ IHRU and the total number of clusters was counted with the time step $\Delta t = t_{tot}/100$. When this number stabilized after about 70 steps we obtained the cluster size distribution as the sum of the distributions calculated over the last 25 time steps by invoking the principle of

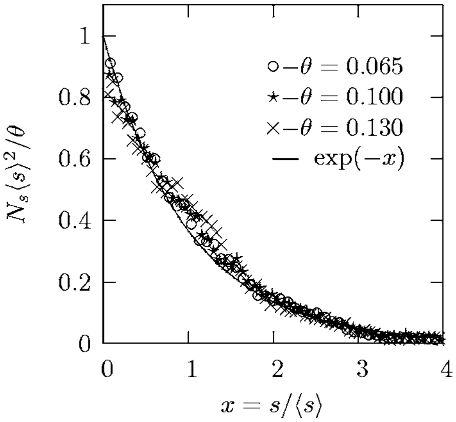

FIG. 4. Monte Carlo simulation data for the scaling function at three coverages within the model explained in the text (symbols) together with the theoretically predicted exponential scaling function (solid line).

ergodicity. The statistics was gathered over eight simulation runs. A typical configuration of the atoms on the surface at the end of the simulation is shown in Fig. 1.

The scaling properties of the distribution are shown in Fig. 4. As can be seen from the comparison of this figure with Fig. 2, the qualitative behavior of the simulated distributions is practically the same as observed experimentally. The same can be said about the behavior of the average cluster size (see Fig. 3), though the agreement became less impressive for larger coverages for which the scaling theory becomes less accurate, as discussed in Sec. II.

IV. DISCUSSION

In this paper we have shown that the equilibrium size distributions of surface clusters can exhibit the scaling behavior similar to that observed in the irreversible growth.[3,5] This may be useful in determination of some equilibrium interaction parameters because scaling distributions improve statistics for their governing parameters, as we illustrated above with the nearest-neighbor interatomic interaction parameter $|V_{NN}^x|$. Our fitted value of this parameter ~0.2 eV, however, looks rather small in comparison with the *ab initio* calculations (~0.8 eV in Ref. 8). If we could prove that this discrepancy is definitely real, then we could have drawn a unequivocal conclusion that the system under consideration is out of equilibrium. However, with the current state of the *ab initio* calculation of the energetics of adsorbates, the above conclusion looks to be premature because the discrepancy may originate from many other sources. First, it should be stressed that the description of deposited structures with the use of simple pair interaction models is a huge oversimplification. This is especially true in connection with metallic systems where the electron collectivization in principle does not allow an adequate pair potential description. Thus the values of pair interactions introduced by us and by some other authors[8,18,19] are only some loosely defined average quantities which describe the attachment and detachment of atoms from different structures.

Another source of discrepancies is the difficulty of *ab initio* calculations of the surface properties caused by the absence of symmetry in the case of the structures under consideration. Therefore instead of the irregular structures observed experimentally, symmetric and periodic structures are used in *ab initio* calculations with some essential parameters to be quite different from those in the experiment. For example, the value $V_{NN}^x \approx -0.8$ eV was calculated with the use of an infinite (2×2) structure corresponding to coverage 50% while the experimental coverages were less than 13%.

Similar discrepancy was found in the case of the Co/Cu(001) heteroepitaxy studied in Ref. 26. While the *ab initio* calculations with a (4×2)-unit cell gave the Co dimer energy 0.74 eV, it was found that the experimentally observed number of clusters is better reproduced in the Monte Carlo simulations with this parameter taken to be 0.2 eV.

The influence of the surface on the values of the interatomic interactions is very essential. For example, in the case of the group-III atoms on the Si(001) surface the NN interatomic interaction may vary from strong and negative (−1.1 eV) along one direction to strong and positive in the orthogonal direction (+0.1 eV).[12] Obviously that this is the consequence of the presence of the surface. Thus the surface anisotropy may introduce repulsive interaction as large as 1.2 eV. The contributions into the repulsion may come from such complicated phenomena as (i) large lattice size misfit between the substrate (the lattice constant $a=0.384$ nm[3]) and the optimum interatomic distance in Ga metal of about 0.244 nm;[20] (ii) the repulsion propagated by the substrate[21,22] (see the analysis of the anisotropic case in Ref. 23) and of the group-III metals on the Si(100) surface in Ref. 19); (iii) the charge transfer between the metallic atoms and the substrate[24] and strong interatomic repulsive Coulomb interactions caused by this transfer[25] which may be an order of magnitude stronger than the forces due to the misfit mentioned above.

In conclusion, we want to point out that irrespective of whether our theory is applicable to the Ga/Si(001) case discussed above, the techniques developed in the present paper should be useful in the development of experimental setups for a reliable determination of some of the parameters describing interactions and kinetics. From this point of view especially promising look the experiments of Refs. 2 and 4. In the latter reference the authors observed the ripening of one-dimensional nanostructures. Presumably, this was because the linear term in the dependence of the chain energy on size—which may be associated with V_{NN}^x in Eq. (3)—can be assessed from Fig. 16 of Ref. 2 to be of about −0.3 eV. This is a large value which makes it natural to suggest that the atoms will tend to assemble first into linear chains and subsequently into 2D clusters, as the energetics of the Ir/W(110) heteroepitaxial system suggests[2] and explicit observations confirm.[4]

We note, however, that a low-temperature phase diagram of the 2D lattice gas contains both the "solid" phase when the surface almost completely covered by the atoms with a small number of vacant sites, and the gaseous phase—an almost empty lattice with a small number of atoms. These phases are separated by the miscibility gap, so there should exist a sufficiently small atomic concentration for the system to be in the equilibrium gaseous phase. Because of the energetics of the heteroepitaxial systems considered in the above references, the equilibrium atomic clusters in this phase will be one-dimensional and their size distribution can in principle be obtained within the experimental setup of Ref. 4 with a smaller number of atoms. The equilibrium size distribution can be obtained by the observation of different cluster configurations and their temporal averaging due to the ergodicity is equivalent to the ensemble averaging.

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