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Equilibrium island size distribution in one dimension revisited: analytical models and Monte Carlo simulations

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Abstract. The island size distribution, at thermodynamic equilibrium, of interacting particles in a one-dimensional lattice-gas model is revisited. A derivation for the exact island size distribution of nearest neighbor interacting particles using the detailed balance principle is proposed and it is shown that it agrees with the distribution obtained by Gambardella *et al* who resorted to the minimization of the free energy (2006 *Phys. Rev.* B **73** 245425). We find that the island size distributions change from an exponential shape to one exhibiting a maximum when repulsive interactions with distant neighbors are considered. In this work we present an analytical model that successfully reproduces the island size distribution obtained from Monte Carlo simulations for both interaction schemes and any coverage.

Keywords: cluster aggregation (theory)

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Contents

1. Introduction

Self-assembled nanostructures have important roles in several technological applications, and are of particular interest for the formation of self-assembled nanowires on semiconductor surfaces [1]. In particular, chains made of hydrogen, bismuth, gallium, and also silicon have been experimentally observed on Si(100) [1]–[4]. Chainlike structures decorating step edges have been additionally found when adatoms are deposited on vicinal surfaces due to the higher binding energy at step sites [5]. It is therefore important to have a theory that accounts for the key factors that determine the resulting structure.

Exact solutions when only first-neighbor interactions are included have been derived, determining all possible configurations of the system [6]–[8]. In particular, Gambardella *et al* [5] derived an analytical expression for the island size distribution of first-neighbor interacting particles under thermodynamic equilibrium, calculating the island free energy as a function of the island step energy, the adsorption energy, the chemical potential, and the configurational entropy. This approach is very suitable to use to calculate island size distributions from just the knowledge of the number of adsorbed particles and the number of islands.

Here we present an alternative derivation of the theoretical equilibrium island size distribution by means of the detailed balance principle. The advantage of following this approach resides in the fact that the island size distribution can be easily obtained from rates of transition between islands of different sizes, and these rates are determined by particle interaction energies and the geometric constraints imposed by the transition dynamics. A similar approach was used to derive the size distribution in the low coverage limit [9]. Here, we apply this approach to carefully derive an exact analytical expression valid for all coverages, where events of island breaking and coalescence play an important role in determining the island size distribution.

We tested the validity of our model for a variety of energies against the outcomes obtained using Monte Carlo simulations, and we found that the resulting island sizes follow an exponential distribution when only first-neighbor interactions are considered

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regardless of the value taken by the particle interaction strength. Our model matches the results previously found, validating all approaches [5]–[8]. However, many experimental works found that the island size distribution show a maximum instead of an exponential shape. Repulsive interactions beyond first neighbors have been proposed in order to reproduce these findings [10, 11]. Taking the advantage of the simplicity of our model, we extended it to include interactions of this type. Our model replicates Monte Carlo results.

2. Equilibrium island size distribution for nearest neighbor interacting particles

The statistical distribution of interacting particles in a one-dimensional substrate can be derived using thermodynamic arguments. Under thermal equilibrium, the general reaction can be expressed as

$$N_n = N_{n-1} + N_1. \tag{1}$$

This equation accounts for the formation of a cluster of size n when a single particle attaches to a cluster of size $n-1$. Priester and Lannoo proposed applying the law of mass action [9] and thus they derived a general expression. In particular, assuming an attractive interaction ε between first-neighbor particles, we can write

$$\frac{c_n}{c_{n-1}c_1} = \exp(\varepsilon/kT), \tag{2}$$

where c refers to concentrations (for example, $c_n = N_n/N$ with N being the number of lattice sites). Equation (2) leads immediately to the following expression for the island density:

$$c_n = c_1[c_1 \exp(\varepsilon/kT)]^{n-1}. \tag{3}$$

This equation provides the island size distribution dependence on ε and c_1.

Using a different thermodynamic argument, an expression for the island size distribution had been derived. Gambardella *et al* [5] expressed the free energy in terms of the island boundary energy, the adsorption energy, the chemical potential, and the entropy term. The minimization of the free energy leads to the island size distribution in terms of the number of adsorbed particles M and the number of islands K (equation (12) in [5]):

$$N_n = K^2(M-K)^{n-1}M^{-n}. \tag{4}$$

Other parameters enter into the model through M and K, allowing for a direct comparison with experiments.

The distribution functions given by equations (3) and (4) are decreasing geometric series. For any distribution of this type, say $c_n = c_1 x^{n-1}$, the density of islands k and the coverage θ can be determined as

$$k = \sum_n c_n = \frac{c_1}{1-x} \tag{5}$$

$$\theta = \sum_n n c_n = \frac{c_1}{(1-x)^2}. \tag{6}$$

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Thus, $x = (\theta - k)/\theta$ and $c_1 = k^2/\theta$ and the distribution can be written as

$$c_n = \frac{k^2}{\theta}\left(\frac{\theta - k}{\theta}\right)^{n-1}, \tag{7}$$

which is equivalent to equation (4) since $c_n = N_n/N$, $k = K/N$, and $\theta = M/N$.

A similar derivation for the distribution function of empty sites or gaps between islands gives

$$f_n = \frac{k^2}{1-\theta}\left(\frac{1-\theta-k}{1-\theta}\right)^{n-1}. \tag{8}$$

Equation (7) is of general validity while equation (3) is only valid for the dilute limit model (DLM). In order to test its limitations, we can compare it with the exact solution for $\varepsilon = 0$, which is straightforward to derive. In this case, we consider that particles are on the substrate at random. Therefore, the probability of having a single-particle island as a function of coverage is given by $\theta(1-\theta)^2$. Similarly, the probability of having an island formed by two particles is $\theta^2(1-\theta)^2$. This argument leads to the following general form:

$$c_n = \theta^n(1-\theta)^2 = c_1\theta^{n-1}. \tag{9}$$

Monte Carlo simulations were carried out using an array of 10 000 sites simulating the support on which particles are deposited. Particles are initially distributed at random and periodic boundary conditions were used to avoid edge effects. The equilibrium configuration for the system is obtained following the standard Metropolis method. Two sites i (occupied) and j (unoccupied) are selected at random. The energy of the actual configuration is calculated. A virtual transfer of a substrate particle i to site j is considered and the energy for the new configuration is calculated and compared with the energy of the initial configuration. If the system gains energy, the exchange is carried out. Otherwise, the exchange is performed with a probability $\exp(-\Delta E/kT)$ where ΔE is now a loss of energy ($\Delta E > 0$). The system evolves with successive jumps until it approaches the equilibrium configuration. We ensure that the system reaches equilibrium by monitoring the island size distribution. The Monte Carlo results presented here are averaged over 100 samples.

In figure 1 we compare, for $\varepsilon = 0$ and a coverage $\theta = 0.3$, the island size distribution given by equation (3)—the diluted limit model (DLM)—the exact solution given by equation (9), and the distribution obtained with a Monte Carlo simulation. Results show that equation (3) is far from being a good approximation. In the inset of figure 1 we present the average island size $\langle n\rangle$ as a function of coverage for $\varepsilon = 0$. Differences between the $\langle n\rangle$ exact values and those derived from the DLM rapidly diverge with coverage. It is apparent that the DLM is, in general, only valid at very low coverages: for example, the relative error in $\langle n\rangle$ for $\theta = 0.3$ is $\sim$13%.

In what follows, on the basis of the detailed balance principle, we will introduce a derivation for the exact distribution valid at any coverage, i.e. when clusters are not distant.

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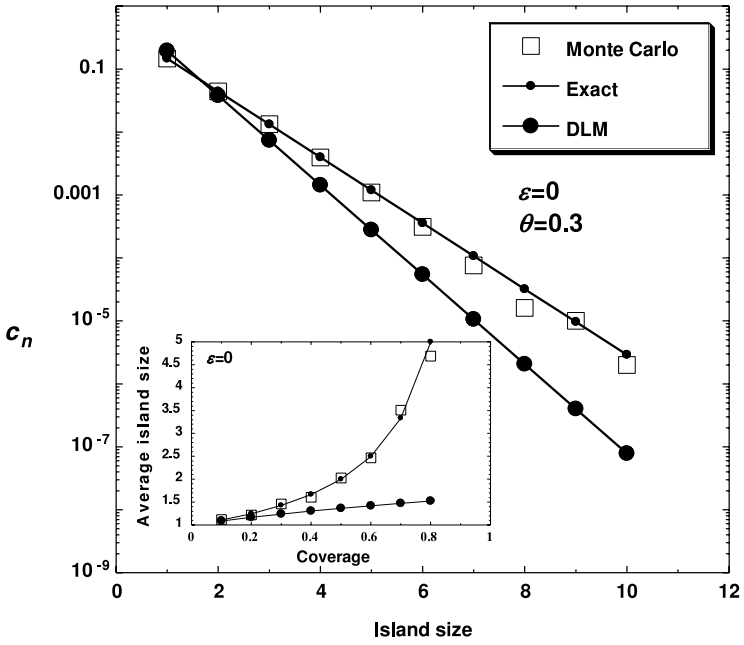

Figure 1. Island size distributions for non-interacting particles and a coverage $\theta = 0.3$. Small filled circles correspond to the exact distribution given by equation (3), large filled circles correspond to the diluted limit model (DLM), and open squares correspond to the distribution obtained with Monte Carlo simulations. The inset shows the average island size as a function of coverage.

3. Derivation of the exact distribution for nearest neighbor interacting particles and any island density

Under thermodynamic equilibrium, the rate of reaction in equation (1) from N_n to $N_{n-1} + N_1$ must be the same as the inverse reaction rate. However, it is expected that, as coverage increases, the attaching or detaching of a particle to or from an island of size n will not always result in an island of size $n+1$ or in a single-particle island. In order to take into account these events in our model we rewrite equation (2) as follows:

$$\alpha c_n = \beta c_{n-1} c_1 \exp(\varepsilon/kT), \tag{10}$$

where we have included two factors, α and β, which suitably incorporate the above mentioned events. The factor α in the left side of equation (10) must take into account that not all particles detaching from islands find empty sites to form single-particle islands. On the other hand, the factor β in the right side of equation (10) must take into account the fact that when a particle sticks to an island of size $n-1$, we do not always find that an island of size n is formed (due to island coalescence). In the DLM, α and β are considered equal to 1.

Since we are working within a lattice-gas framework, particles can only diffuse or jump to an unoccupied site. It is also expected that, as the coverage increases, the number of unoccupied sites at which a landing particle forms a single-particle island decreases. Among these sites, those neighboring islands are not included because a

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particle incorporated at this type of site will become part of an already existing island. Consistently, the factor α can be expressed as follows:

$$\alpha = 1 - \theta - 2k + f_1, \tag{11}$$

where f_1 is the density of gaps of size 1. In principle, an island contributes by reducing α by two sites, those neighboring its two ends. However, every gap of only one site implies that we have counted the same site twice and thus the number of sites neighboring islands is $2k - f_1$.

The factor β in the right side of equation (10) is a correction that takes into account the incorporations into single-site gaps. Indeed, if a particle lands in a single-site gap, two islands merge instead of incrementing by 1 the size of an island. The probability of having a single-site gap neighboring a cluster is f_1/k and then β takes the form

$$\beta = 1 - f_1/k. \tag{12}$$

From equations (10), (11), and (12), the following island size distribution can be derived:

$$c_n = c_1 \left(\frac{c_1(1 - f_1/k)\exp(\varepsilon/kT)}{1 - \theta - 2k + f_1} \right)^{n-1}. \tag{13}$$

We know that $c_1 = k^2/\theta$ (see equation (7)) and $f_1 = k^2/(1-\theta)$ (see equation (8)), so equation (13) reduces to

$$c_n = c_1 \left(\frac{k^2 \exp(\varepsilon/kT)}{\theta(1 - \theta - k)} \right)^{n-1}. \tag{14}$$

The form of equation (13) is a decreasing geometric series. Therefore, equations (5)–(7) are valid with

$$x = \frac{k^2 \exp(\varepsilon/kT)}{\theta(1 - \theta - k)}. \tag{15}$$

For given θ and ε, we can proceed by finding the value of k connecting equations (5), (6), and (15):

$$\frac{k}{\theta} = 1 - x = 1 - \frac{k^2 \exp(\varepsilon/kT)}{\theta(1 - \theta - k)}. \tag{16}$$

This equation allows us to determine k. Once k is known, the rest of the relevant parameters can be directly obtained. In the case already studied, corresponding to $\varepsilon = 0$ and $\theta = 0.3$, equation (16) leads to $k = 0.21$; then $c_1 = 0.147$ and $x = 0.3$. The resulting island size distribution is the exact one. Interestingly, equation (16) can be arranged as

$$\varepsilon = kT \ln \left(\frac{(\theta - k)(1 - \theta - k)}{k^2} \right). \tag{17}$$

This is equivalent to equation (10) of [5] showing that the proposed derivation leads to the exact solution.

We have tested this model for a variety of energies and we found that, regardless of the strength of the attractive interaction, the resulting island size distribution is always a monotonically decreasing distribution as predicted by equation (14), against what would

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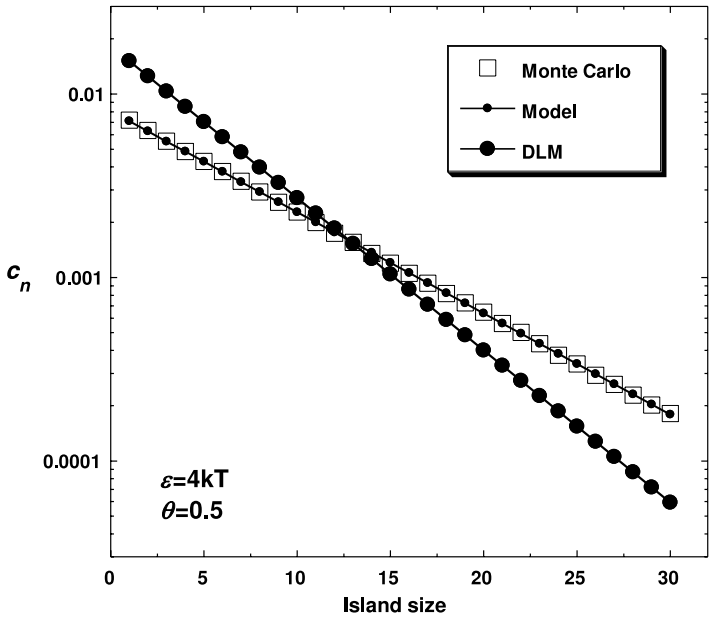

Figure 2. Island size distributions for interacting particles with first-neighbor interaction energy $\varepsilon = 4kT$ and a coverage $\theta = 0.3$. Small filled circles correspond to the exact distribution given by equation (3), large filled circles correspond to the diluted limit model (DLM), and open squares correspond to the distribution obtained with Monte Carlo simulations.

be expected from the attractive nature of the interaction. Equation (14) is the exact distribution for a substrate of infinite size. This implies that, as the attractive interaction ε increases and then the size of the islands grows accordingly, the Monte Carlo simulation could present finite size effects. In figure 2, we show results for an attractive interaction $\varepsilon = 4kT$ using a substrate of 10 000 sites in order to ensure that wider islands are small compared with the substrate size.

4. Extending interactions beyond first neighbors

Experimental results obtained in [5] show a monomodal island size distribution instead of the monotonic one predicted with equation (14). It has been argued that the origin of this discrepancy can be explained if the epitaxial strain resulting from the mismatch between the islands and the substrate is properly incorporated [10, 11]. As a consequence of substrate stress, the energy for adding or removing a particle from an island depends on its size. This dependence can be properly taken into account by including interactions with all particles of the island. It is expected that each particle added to the island would increase the strain, so the interactions beyond first neighbor must be of a repulsive nature.

Exploiting the simplicity of the analytical derivation presented, we extended it to include interactions beyond first neighbors to check the effects over the island size distributions. Following [11] and for sake of simplicity, we will adopt a repulsive potential of the form Q/r and test the model validity against Monte Carlo simulation results.

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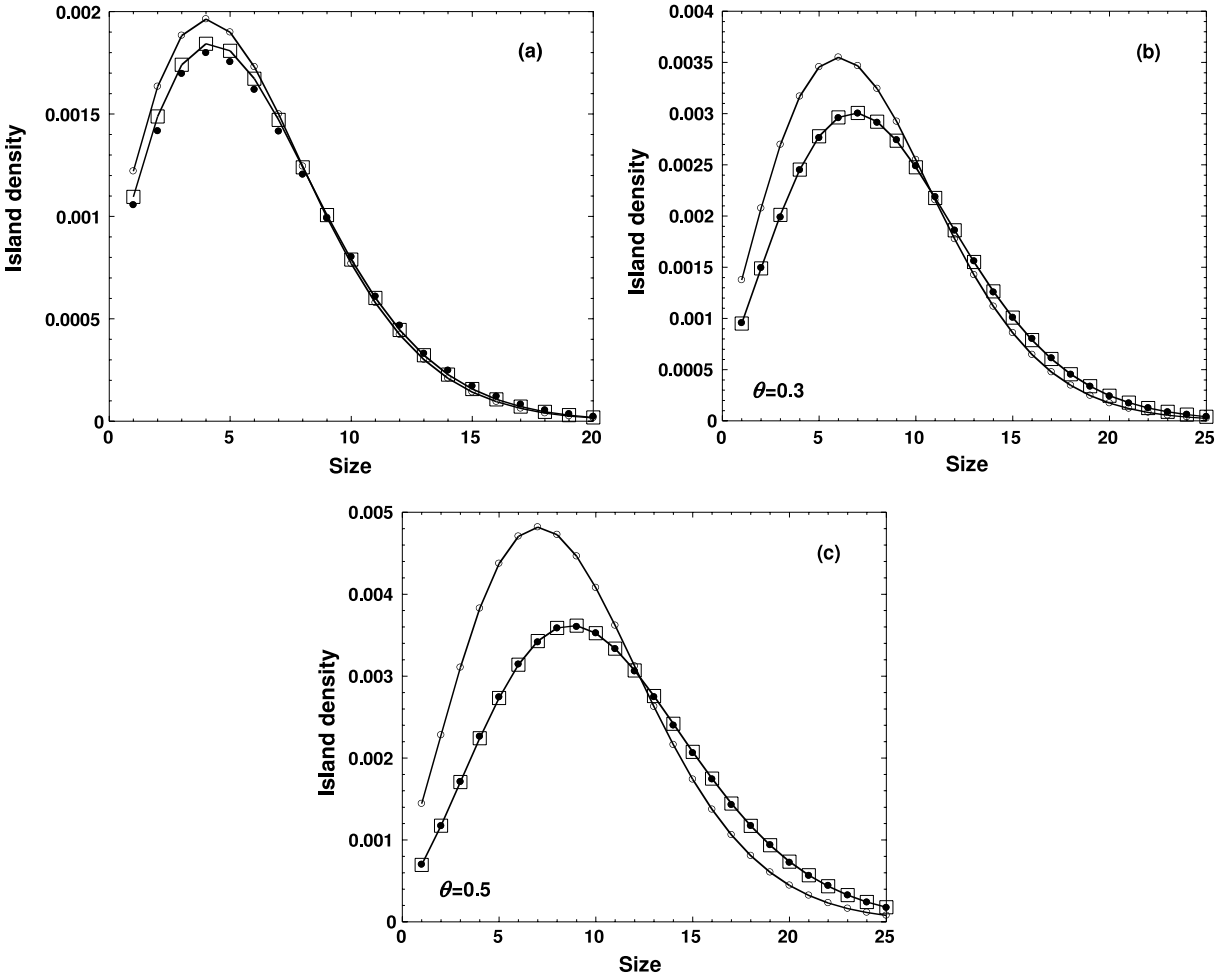

Figure 3. Island size distributions including interactions beyond first neighbors according to equation (18) with $\varepsilon/kT = 7$, $Q/kT = 0.3$ and (a) $\theta = 0.1$, (b) $\theta = 0.3$, and (c) $\theta = 0.5$. Filled circles correspond to the exact distribution given by equation (20), open circles correspond to the diluted limit model (DLM), and open squares correspond to the distribution obtained with Monte Carlo simulations.

We can easily modify equation (14) to include the above mentioned potential expressing the energy gained when a particle is incorporated into an island of size n as follows:

$$E_n = \varepsilon - \sum_{i=2}^{n} Q/i. \tag{18}$$

The second term on the right-hand side is the repulsive energy for a particle that is added to an island of size n. A recursive equation for determining c_n can be readily expressed as

$$c_n = \frac{c_1 c_{n-1}}{1-\theta-k} \exp(E_{n-1}/kT). \tag{19}$$

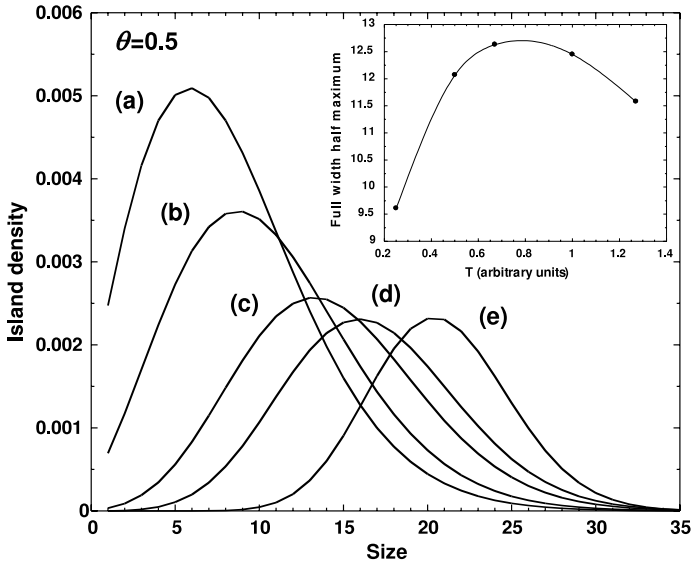

Figure 4. Island size distributions including interactions beyond first neighbors according to equation (20) for $\theta = 0.5$. Distribution (b) was obtained with $\varepsilon/kT_{\rm ref} = 7$, $Q/kT_{\rm ref} = 0.3$; (a) corresponds to $T = 1.27T_{\rm ref}$, (c) to $T = 0.67T_{\rm ref}$, (d) to $T = 0.5T_{\rm ref}$, and (e) to $T = 0.25T_{\rm ref}$. The inset shows the full width at half-maximum of the distributions as a function of temperature.

With equations (18) and (19) a general form can be derived:

$$c_n = c_1 \left(\frac{c_1 \exp[(\varepsilon + 2Q)/kT]}{1 - \theta - k} \right)^{n-1} [\exp[-(QH_{n-1})/kT]^n \tag{20}$$

where H_n is the harmonic function given by

$$H_n = \sum_{i=1}^{n} \frac{1}{i} = \ln(n) + \gamma + \frac{1}{2n}, \tag{21}$$

and γ is the Euler–Mascheroni constant ($\approx$0.577).

Figure 3 shows results for island size distributions for $\varepsilon/kT = 7$ and $Q/kT = 0.3$ and three coverages. It is readily observed that the DLM can only be applied for low coverages. As coverage increases, the distribution is very much affected and the DLM is no longer a good approximation. In particular, for $\theta = 0.3$ equation (20) shows a maximum around 7 according to the results obtained before [5, 11]. Calculations of the configurational energy differences in the Monte Carlo simulations involve adding the attractive interactions to nearest neighbors and subtracting the repulsive ones between particles beyond first neighbors as expressed in equation (18). In these calculations we carefully took into account events in which a particle with two first neighbors is removed, breaking the island into two pieces, and also the reverse process in which a particle is added to a hole between two neighboring islands, merging them into a single large island. Monte Carlo results confirm the correctness of the expression given by equation (20). Following this method, closed forms for other potentials could be readily found.

Using our analytical expression for island size distribution, we check how distribution shapes change with temperature. As can be seen in figure 4, distributions tend to a

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Gaussian shape and become sharper at low temperatures [8, 9]. As a final remark, we stress that, although the width of the distribution tends to decrease with temperature, it does not do it strictly monotonically [7], at least for the repulsive potential tested in this work.

5. Conclusions

In this work we presented an analytical model based on the detailed balance principle that successfully reproduces the island size distribution obtained with Monte Carlo simulations for any coverage and nearest neighbor interacting particles in 1D. We found that in this case our analytical expression agrees with the distribution obtained by Gambardella *et al* that was found by minimizing the system free energy. We extended the interaction scheme to more distant neighbors using a repulsive potential and we also derived the island size distribution showing that it changes from an exponential shape to one exhibiting a maximum, as experimentally observed. Again, our findings reproduce the results obtained using Monte Carlo simulations.

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