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Island size distributions in submonolayer growth: Prediction by mean field theory with coverage dependent capture numbers

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We show that mean field rate equations (MFRE) for submonolayer growth with hit and stick aggregation can successfully predict the island size distributions (ISDs) in the precoalescence regime if the full dependence of capture numbers on both the island size and the coverage is taken into account. This is demonstrated by comparison of the integrated MFRE with results from extensive kinetic Monte Carlo simulations. The attempt to use various simplified expressions for the capture numbers in the integration of the MFRE turns out to be insufficient to yield a good description of the ISD.

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The kinetics of submonolayer nucleation and island growth during the initial stage of epitaxial thin-film growth has been studied intensively both experimentally and theoretically (for reviews, see Refs. 1–3). A good understanding of this kinetics assists in tailoring self-organized nanostructures and thin-film devices for specific needs. Mean field rate equations (MFRE) (Ref. 4) successfully predict important features such as the scaling behavior of the density of stable islands with respect to the $\Gamma = D/F$ ratio of the adatom diffusion rate D and incoming flux F.[5–8] They seem to fail, however, to predict correctly the number densities n_s of islands composed of s atoms, i.e., the island size distributions (ISDs).[9] In this connection, Ratsch and Venables[10] addressed a still open question: whether the MFRE are successful in describing the precise shape of the ISD, if the correct dependence of the capture numbers $\sigma_s(\Theta)$ on both s and the coverage Θ were taken into account. The answer to this question is not obvious since the MFRE with correct capture numbers $\sigma_s(\Theta)$ still neglect (i) many-particle correlation effects,[11] (ii) spatial fluctuations in shapes and capture zones of islands, and (iii) coalescence events that, despite rare in the early stage growth, could have a significant influence.

Various theoretical approaches have been developed in the past for obtaining appropriate analytical formulas or approximate numerical results for the $\sigma_s(\Theta)$ (for details, see Refs. 1 and 10, and references therein). These approaches focus mostly on the low-temperature case with critical size $i = 1$, i.e., the case when already dimers can be considered as stable (on a time scale, where the ISD in the initial growth regime is formed). Some results for higher i were reported in Ref. 1 and were generated mainly in connection with a geometry-based simulation strategy.[12] The roughest approach for $i = 1$ is to neglect the Θ dependence and to use just two numbers, σ_1 for the adatoms and an average number $\bar{\sigma}$ for all stable islands with $s \geq 2$ and to fit these numbers to give best agreement with simulated or measured data. Alternatively, simulated capture numbers for various s at a fixed coverage Θ have been considered[13] and used in the analysis of experiments.[14] As shown in Fig. 1, however, neither of these approaches as well as a more sophisticated self-consistent treatment[9,15] is successful in providing a good description of the ISD as obtained from kinetic Monte Carlo (KMC) simulations. Therefore a semiempirical form of the ISD (Ref. 16) is often used in the analysis of experiments.[17,18] It is interesting to note that a semiempirical form has been suggested recently also for the capture zone distribution in Ref. 19. The parameters used in this form, however, are controversially discussed.[20,21]

A first numerical study for computing coverage dependent capture numbers has been performed in Refs. 22 and 23 using a level set method. Integration of the MFRE with the obtained capture numbers gave quantitative agreement with KMC results for the island density N but the statistics was insufficient to achieve conclusive answers with respect to the ISD. For taking into account the correlation between s and the size of capture zone areas, i.e., that larger islands tend to exhibit larger capture zones, a generalization of the MFRE toward an evolution equation for the joint probability of island size and capture area was setup.[24–26] This, however, had to be done at the expense of introducing additional parameters for considering nucleation events inside the capture zones.

In this study we compute the capture numbers $\sigma_s(\Theta)$ as a function of both the island size s and the coverage Θ by performing extensive KMC simulations. We show that based on these functions the ISD for growth kinetics with hit and stick aggregation is well predicted by the MFRE in the growth regime before coalescence. We discuss simplified forms of the capture numbers $\sigma_s(\Theta)$ with respect to predicting the ISD, which could render an analytical treatment of the problem possible.

The MFRE for a situation at low temperatures (no reevaporation) with a critical nucleus of size $i = 1$ and consideration of direct impingement of arriving atoms at islands are

$$\frac{dn_1}{dt} = (1-\Theta)F - 2D\sigma_1 n_1^2 - Dn_1 \sum_{s>1} \sigma_s n_s - 2F\kappa_1 n_1 - F\sum_{s>1} \kappa_s n_s, \qquad (1)$$

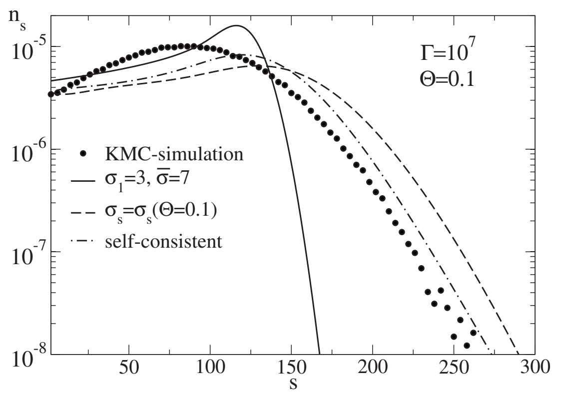

FIG. 1. Island size distribution obtained from KMC simulation in comparison with ISDs calculated from an integration of the MFRE using three different approximations for the $\sigma_s(\Theta)$.

$$\frac{dn_s}{dt} = Dn_1(\sigma_{s-1}n_{s-1} - \sigma_s n_s) + F\kappa_{s-1}n_{s-1} - F\kappa_s n_s, \quad s = 2,3,\ldots \tag{2}$$

These equations refer to the growth regime, where coalescence events of islands should be negligible, and it is presumed that only single adatoms are mobile and that atom movements between the first and second layer can be disregarded. Moreover, adatoms arriving on top of an island are not counted, i.e., s in a strict sense refers to the number of substrate sites covered by an island (or the island area). Accordingly, the deposition flux F of adatoms in Eq. (1) has to be restricted to the uncovered fraction $(1-\Theta)$ of the substrate area. The terms $2D\sigma_1 n_1^2$ and $F\kappa_1 n_1$ describe the nucleation of dimers due to attachment of two adatoms by diffusion and due to direct impingement, respectively. The term $Dn_1\sigma_s n_s$ describes the attachment of adatoms to islands of size $s>1$ and $F\kappa_s n_s$ the direct impingement of deposited atoms to boundaries of islands with size s. Dividing Eqs. (1) and (2) by F leads to evolution equations with the coverage $\Theta = Ft$ as independent variable and to a replacement of D by $\Gamma = D/F$ on the right-hand side.

Our KMC simulations are performed with an exact continuous-time algorithm and periodic boundary conditions on a square lattice with $L\times L = 8000\times 8000$ sites. The lattice constant is set to unity. We consider a kinetics with "hit and stick" aggregation, which implies fractal island morphologies.[1–3] To calculate the capture numbers σ_s at the coverage Θ, we use the following procedure: each simulation run is stopped at coverage Θ and the number densities $n_s = N_s/L^2$, $s=1,2,\ldots$ are determined, where N_s are the numbers of monomers ($s=1$) and islands ($s>1$). Then the simulation is continued for a long-time interval T without deposition and the following additional rules: (i) when an adatom is attaching to an island of size $s>1$, a counter M_s for such attachments is incremented and the adatom thereafter repositioned at a randomly selected site of the free substrate area (i.e., a site which is neither covered nor a nearest neighbor of a covered site); (ii) when two adatoms form a dimer, a counter M_1 for these nucleation events is incremented and the two adatoms thereafter repositioned randomly as described in (i). In this way a stationary state is maintained at the coverage Θ. Using the counters, the mean times $\tau_s = T/M_s$, $s=1,2,\ldots$, for the respective nucleation and attachment events are determined. Given these times, the capture numbers σ_s are calculated by equating $D\sigma_s n_1 n_s$, $s=1,2,\ldots$ with $1/\tau_s$, yielding $\sigma_s = 1/[Dn_1 n_s \tau_s]$. Averaging the σ_s over many simulation runs (configurations) finally gives $\sigma_s(\Theta)$. The $\kappa_s(\Theta)$ are determined from the lengths of the islands boundaries, which are simultaneously monitored during the simulation and averaged for each size s.

Overall the functions $\sigma_s(\Theta)$ and $\kappa_s(\Theta)$ were obtained for 57 different Θ values in the range 0.005–0.2 and a large number of island sizes for each value of Θ, ranging up to 1000 values for the largest Θ. The typical number of nucleation/attachment events for each Θ value was 10^8.

Figure 2(a) shows results for $\sigma_s(\Theta)$ as a function of s for four different fixed Θ at $\Gamma = 10^7$. For large s we find a linear dependence of $\sigma_s(\Theta)$ on s at all coverages, which can be explained[1] by noting that the $\sigma_s(\Theta)$ become proportional to the mean capture zone areas A_s. Since a double-sized capture zone gives on average rise to a double-sized island, it holds $A_s \sim s$ and hence $\sigma_s \sim s$. The asymptotic behavior can be described by $\sigma_s(\Theta) \sim a(\Theta)s + b(\Theta)$, where the slope $a(\Theta)$ is an increasing and the offset $b(\Theta)$ a decreasing function of Θ, see Fig. 2(b). For small s, a nonlinear dependence of $\sigma_s(\Theta)$ on s is in agreements with earlier findings.[15] As shown in the inset of Fig. 2(a), the direct capture numbers $\kappa_s(\Theta)$ have also a linear dependence on s but are approximately independent of Θ, i.e., $\kappa_s(\Theta) \simeq s$. In Fig. 2(c) we show the capture number $\sigma_1(\Theta)$ related to nucleation events and the mean capture number $\bar{\sigma}(\Theta) = \Sigma_{s=2}^{\infty} \sigma_s(\Theta) n_s / N$, where $N = \Sigma_{s=2}^{\infty} n_s$. These functions are important when considering the scaled capture numbers $\sigma_s(\Theta)/\bar{\sigma}(\Theta)$ as function of the scaled island size $s/\bar{s}(\Theta)$, where $\bar{s}(\Theta) = \Sigma_{s=2}^{\infty} s n_s / N \cong 4.7 + 818\Theta$ at $\Gamma = 10^7$ here.[27] Looking at the scaled capture numbers $\sigma_s/\bar{\sigma}$ at fixed $\Theta = 0.1$ for various Γ in Fig. 2(d), we find no collapse onto one curve in the Γ range $10^5 - 10^8$ studied here. It is possible that for larger Γ a "scaling limit" with a data collapse emerges, which would allow one to apply the analytical theory for the scaled ISD developed by Bartelt and Evans.[13] From the data in Fig. 2(d) one can infer that much larger Γ values than 10^8 are necessary to approach a possible limit. Despite of the fact that an analogous investigation for such large Γ values would require a tremendous additional computational effort, we would like to note that the analysis of the scaled ISD is not the primary goal of this work but the question whether an integration of the MFRE with suitable capture numbers can predict the ISD for Γ values as typically present in experiments.

By combining the linear function for large s with a polynomial at small s to take into account the nonlinearity, we fitted the curves in Fig. 2(a) and used these fits to integrate the MFRE, Eqs. (1) and (2). The data for the resulting MFRE-ISDs in Figs. 3(a) and 3(b) are one of our key findings. As shown in Fig. 3(a), the MFRE-ISD (solid lines) is for all coverages in the precoalescence regime in excellent agreement with the corresponding KMC-ISD (symbols) obtained from the KMC simulations. A variation in Γ does not affect the quality of agreement, as can be seen from Fig. 3(b), where we plot the scaled ISDs $n_s\bar{s}^2/\Theta$ versus $s/\bar{s}$ for a

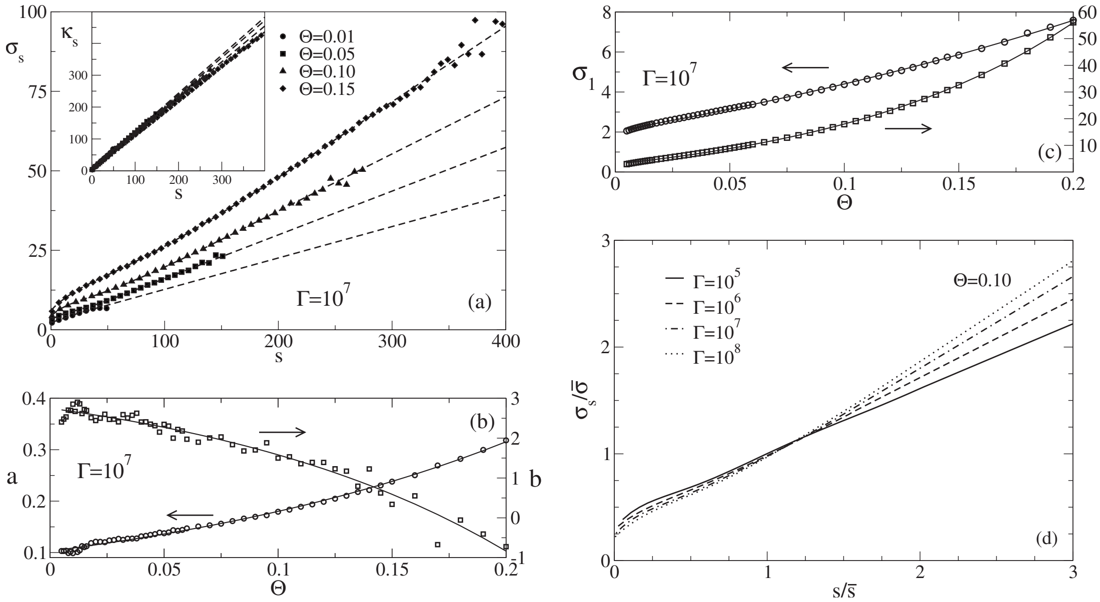

FIG. 2. (a) Dependence of the capture numbers $\sigma_s(\Theta)$ on s for four different fixed coverages; the inset shows the corresponding $\kappa_s(\Theta)$. (b) The coefficients a and b of the asymptote $\sigma_s(\Theta) \sim a(\Theta)s+b(\Theta)$, and (c) σ_1 and $\bar{\sigma}$ as functions of Θ. For a convenient extraction of the data in (b) and (c) the following fit function can be used (solid lines): $a=0.103\,\exp(5.6\Theta)$, $b=3.85-1.1\,\exp(7.26\Theta)$, $\sigma_1=-4.5+6.55\,\exp(3.05\Theta)$, and $\bar{\sigma}(\Theta)=-6.8+9.8\,\exp(9.3\Theta)$. (d) Scaled capture number $\sigma_s/\bar{\sigma}$ versus $s/\bar{s}$ at fixed $\Theta=0.1$ for various Γ values.

fixed coverage $\Theta=0.1$ and four different Γ. Moreover, one can infer from this figure that the scaled ISDs tends to approach a limiting master curve when $\Gamma \to \infty$. For comparison with earlier results in the literature, we show in the inset of Fig. 3(b) the scaled ISDs in the more common double-linear plot instead of the linear-log representation used otherwise in Figs. 1, 3(a), 3(b), and 4. We chose this linear-log representation to show that the MFRE capture the behavior also correctly in the wings at very small ($s \ll \bar{s}$) and very large island sizes ($s \gg \bar{s}$). In fact, the agreement is seen over about 4 orders of magnitude of n_s in Fig. 3(a). A χ^2 test with a standard significance level of 5% is passed for all $\theta \leq 0.18$, which means the MFRE can be safely used up to coverages of at least 20%. This demonstrates that the approximations involved in the MFRE are appropriate to predict the ISD with high accuracy for the hit and stick aggregation considered here.

So far we have used the complete functional form for $\sigma_s(\Theta)$ and $\kappa_s(\Theta)$. The question arises whether all details seen in Fig. 2(a) are necessary with respect to a good prediction of the ISD. To this end we discuss the following simplifications: (i) all κ_s are set to zero, (ii) the $\sigma_s(\Theta)$ are replaced by $\sigma_1(\Theta)$ for $s=1$ and $\bar{\sigma}(\Theta)$ for $s \geq 2$ [and analogously for the $\kappa_s(\Theta)$], and (iii) the asymptotics $\sigma_s(\Theta) \sim a(\Theta)s+b(\Theta)$ is used for all $s \geq 2$ while we keep the $\sigma_1(\Theta)$ [again the analogous procedure is used for the $\kappa_s(\Theta)$].

Figure 4 shows the MFRE-ISD resulting from these simplifications. Neglecting the κ_s in Eqs. (1) and (2), the ISD is again well predicted, see the dashed line. For larger Γ the agreement becomes even better (not shown). When neglecting the s dependence [case (ii)] the MFRE-ISD has a maximum still close to the KMC-ISD but its width is much smaller than that of the KMC-ISD. The width of the respective scaled distribution tends to zero for $\Gamma \to \infty$. Let us re-

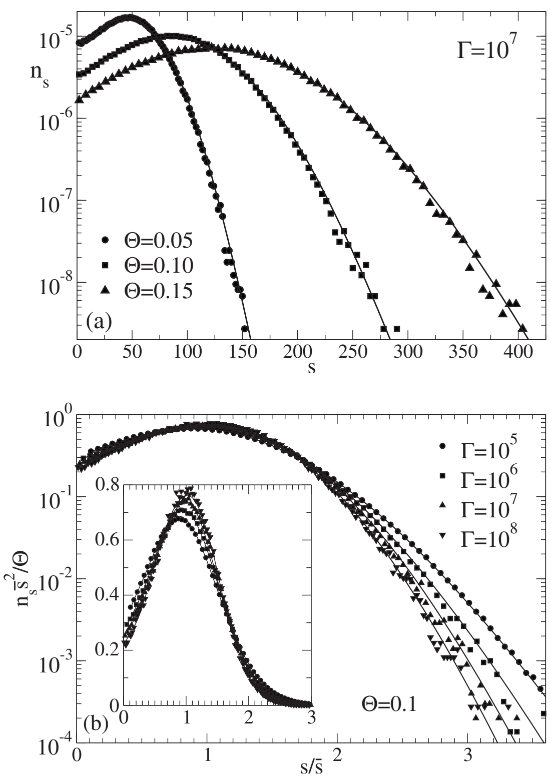

FIG. 3. (a) Island size distributions for three different coverages at fixed $\Gamma=10^7$ and (b) scaled ISDs for four different Γ. The inset in (b) shows the scaled ISDs in a double-linear representation. The symbols mark the results from the KMC simulations and the solid lines the results obtained from integrating the MFRE, Eqs. (1) and (2), with $\sigma_s(\Theta)$ and $\kappa_s(\Theta)$ determined by KMC simulations (see text).

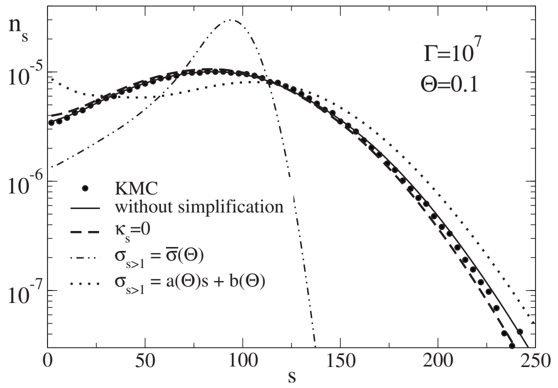

FIG. 4. Island size distribution for $\Theta=0.1$ from the KMC simulation in comparison with the MFRE results when using different simplifications with respect to the functional form of the capture numbers (see text).

mind that we already showed in Fig. 1 that a full neglect of the Θ dependence also does not yield a good ISD. In case (iii) the MFRE-ISD is also poor in comparison with the KMC-ISD. The MFRE-ISD shows a second maximum at $s=2$, which is caused by the fact that the linear relationship underestimates the $\sigma_2(\Theta)$ value, leading to a higher lifetime and correspondingly larger concentration of dimers. Generally speaking, a linear relationship between $\sigma_s(\Theta)$ and s does not cover the small s behavior but, as one would expect, it gives a fair account of the shape of the ISD for large s.

In summary, we have demonstrated that an integration of the standard MFRE with coverage dependent capture numbers yields an MFRE-ISD that for hit and stick aggregation is in excellent agreement with the KMC-ISD. The full dependence of the capture numbers on both the island size and the coverage was determined from extensive KMC simulations and the functional form was analyzed in detail. Despite the fact that a linear dependence on the island size holds over almost the entire s range, the nonlinear behavior is crucial for a good account of the ISD. This implies that it will be difficult to find simple functions, which one could use in an analytical continuum approach for the scaled ISD.[13]

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