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

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We show that mean-field rate equations for submonolayer growth can successfully predict island size distributions in the pre-coalescence regime if the full dependence of capture numbers on both the island size and the coverage is taken into account. This is demonstrated by extensive Kinetic Monte Carlo simulations for a growth kinetics with hit and stick aggregation. A detailed analysis of the capture numbers reveals a nonlinear dependence on the island size for small islands. This nonlinearity turns out to be crucial for the successful prediction of the island size distribution and renders an analytical treatment based on a continuum limit of the mean-field rate equations difficult.

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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 \cite{1,2}). A good understanding of this kinetics assists in tailoring self-organized nanostructures and thin film devices for specific needs. Mean-field rate equations (MFRE) \cite{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 $F$. They seem to fail, however, to predict correctly $n(\Theta)$ (for reviews, see \cite{16}). They seem to fail, however, to predict correctly $n(\Theta)$ (for reviews, see \cite{16}).

Various theoretical approaches have been developed in the past for obtaining appropriate analytical formulae or approximate numerical results for the $\sigma_s(\Theta)$ (for details, see \cite{1,10} and references therein). These approaches focus 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). The roughest approach is to neglect the $\Theta$ dependence and to use just two numbers, $\sigma_1$ 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 $\Theta$ have been considered \cite{10} and used in the analysis of experiments \cite{17}. As shown in Fig. 1, however, neither of these approaches as well as a more sophisticated self-consistent treatment \cite{9,14} is successful in providing a good description of the ISD as obtained from KMC simulations. A first numerical study for computing coverage dependent capture numbers has been performed in \cite{16,18} 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 towards an evolution equation for the joint probability of island size and capture area was set up \cite{18,19}. This, however, had to be done at the expense of introducing additional parameters for considering nucleation events inside the capture zones.

In this Letter we compute the capture numbers $\sigma_s(\Theta)$ as a function of both the island size $s$ and the coverage $\Theta$. We show that mean-field rate equations for submonolayer growth can successfully predict island size distributions in the pre-coalescence regime if the full dependence of capture numbers on both the island size and the coverage is taken into account. This is demonstrated by extensive Kinetic Monte Carlo simulations for a growth kinetics with hit and stick aggregation. A detailed analysis of the capture numbers reveals a nonlinear dependence on the island size for small islands. This nonlinearity turns out to be crucial for the successful prediction of the island size distribution and renders an analytical treatment based on a continuum limit of the mean-field rate equations difficult.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1}
\caption{Island size distribution obtained from KMC simulation in comparison with ISDs calculated from an integration of the MFRE using three different approximations for the $\sigma_s(\Theta)$.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2}
\caption{Island size distribution obtained from KMC simulation in comparison with ISDs calculated from an integration of the MFRE using three different approximations for the $\sigma_s(\Theta)$.}
\end{figure}
when two adatoms form a dimer, a counter
adatom thereafter repositioned at a randomly selected
M
(i) when an adatom is attaching to an island of size
s >
average Θ, we use the following procedure: Each simulation
the numbers of monomers (s
boundaries of islands with size
and
scribes the attachment of adatoms to islands of size
s >
s to unity. To calculate the capture numbers
Γ =
F
Θ =
F t
(2) by
F
with
tions for “hit and stick” aggregation on a square lattice
islands are

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

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

These equations refer to the growth regime, where coa-
escence 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 is 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 - Θ) 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
Θ = Ft as independent variable and to a replace of D by
Γ = D/F on the right hand side.

Our KMC simulations are performed with an exact
continuous-time algorithm and periodic boundary condi-
tions for “hit and stick” aggregation on a square lattice
with \(L \times L = 8000 \times 8000\) sites. The lattice constant is set
to unity. To calculate the capture numbers \(\sigma_s\) at the cover-
age 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 following 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 cover-
age Θ. Using the counters, the mean times \(\tau_s = T/M_s\),
\(s = 1, 2, \ldots\) for the respective nucleation and attach-
ment events are determined. Given these times, the cap-
ture numbers \(\sigma_s\) are calculated by equating
\(D\sigma_s n_1 n_s\),
\(s = 1, 2, \ldots\) with \(1/\tau_s\), yielding \(\sigma_s = 1/[Dn_1 n_s \tau_s]\).
Aver-
aging the \(\sigma_s\) 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 simultane-
ously 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 \(\Theta\) values in the range 0.005–0.2 and a large
number of island sizes for each value of \(\Theta\), ranging
up to 1000 values for the largest \(\Theta\). The typical number of
nucleation/attachment events for each \(\Theta\) value was
\(10^8\).

Figure 2a) shows results for \(\sigma_s(\Theta)\) as a function of
s for four different fixed \(\Theta\) at \(\Gamma = 10^7\). For large s

![Figure 2](attachment:image_url)

FIG. 2: (a) Dependence of the capture numbers \(\sigma_s(\Theta)\) on s
for four different fixed coverages; the inset shows the corre-
sponding \(\kappa_s(\Theta)\). (b) The coefficients \(a\) and \(b\) of the asymptote
\(\sigma_s(\Theta) \sim a(\Theta) s + b(\Theta)\), and (c) \(\sigma_1\) and \(\tilde{\sigma}\) as functions of \(\Theta\). For
a convenient extraction of the data in (b) and (c) the follow-
ing 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
\(\tilde{\sigma}(\Theta) = -6.8 + 9.8 \exp(9.3\Theta)\).
we find a linear dependence of $\sigma_s(\Theta)$ on $s$ at all coverages, which can be explained 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 $\Theta$, see Fig. 2(a). For small $s$, a nonlinear dependence of $\sigma_s(\Theta)$ on $s$ is found. 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 $\Theta$, i.e. $\kappa_s(\Theta) \approx \sim 0$. In Fig. 2(b) we show the capture number $\kappa_s(\Theta)$ related to nucleation events and the mean capture number $\bar{\kappa}(\Theta) = \sum_{s=2}^{\infty} \sigma_s(\Theta)n_s/N$, where $N = \sum_{s=2}^{\infty} n_s$. These functions are important when considering the scaled capture numbers $\sigma_s(\Theta)/\bar{\kappa}(\Theta)$ as function of the scaled island size $s/\bar{s}(\Theta)$, where $\bar{s}(\Theta) = \sum_{s=2}^{\infty} s n_s/N \approx 4.7 + 818 \Theta$ at $\Gamma = 10^7$ (and analogously for the $\kappa_s(\Theta)$).

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 equations (1) and (2). The data for the resulting MFRE-SDs in Figs. 3a,b are one of our key findings. As shown in Fig. 3a, the MFRE-SD (solid lines) is for all coverages in the precocloence regime in excellent agreement with the corresponding KMC-SD (symbols) obtained from the KMC simulations. A variation of $\Gamma$ does not affect the quality of agreement, as can be seen from Fig. 3b, where we plot the scaled ISDs $n_s\bar{s}^2/\Theta$ versus $s/\bar{s}$ for a fixed coverage $\Theta = 0.1 \Gamma = 10^7$. Consequently, the agreement becomes even better (not shown). For comparison with earlier results in the literature, we show in the inset of Fig. 3a the KMC simulations. A variation of $\Gamma$ does not affect the quality of agreement, as can be seen from Fig. 3b, where we plot the scaled ISDs $n_s\bar{s}^2/\Theta$ versus $s/\bar{s}$ for a fixed coverage $\Theta = 0.1 \Gamma = 10^7$. Moreover, one can infer from this figure that the scaled ISDs tend 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. 3a, the scaled ISDs in the more common double-linear plot instead of the linear-log representation used otherwise in Figs. 1, 3a,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 four orders of magnitude of $n_s$ in Fig. 3a. 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 $\kappa_s$ 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-SD resulting from these simplifications. Neglecting the $\kappa_s$ in Eqs. (1) and (2), the ISD is again well predicted, see the dashed line. For increasing $\Gamma$ the agreement becomes even better (not shown). When neglecting the $s$-dependence (case (ii)) the MFRE-SD has a maximum still close to the KMC-SD.
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 remind that we already showed in Fig. 1 that a full neglect of the $\Theta$ 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 [16].

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