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# Reversible island nucleation and growth with anomalous diffusion

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ABSTRACT

Motivated by recent experiments on submonolayer organic film growth with anomalous diffusion, a general rate-equation (RE) theory of submonolayer island nucleation and growth was developed (Amar and Semaan, 2016) [23], which takes into account the critical island-size $i$, island fractal dimension $d_f$, substrate dimension $d$, and diffusion exponent $\mu$, and good agreement with simulations was found for the case of irreversible growth corresponding to a critical island-size $i = 1$ with $d = 2$. However, since many experiments correspond to a critical island-size larger than 1, it is of interest to determine if the RE predictions also hold in the case of reversible island nucleation with anomalous diffusion. Here we present the results of simulations of submonolayer growth with $i = 2$ ($d = 2$) which were carried out for both the case of superdiffusion ($\mu > 1$) and subdiffusion ($\mu < 1$) as well as for both ramified islands ($d_f \simeq 2$) and point-islands ($d_f = \infty$). In the case of superdiffusion, corresponding to 'hot' freshly deposited monomers, excellent agreement is obtained with the predictions of the generalized RE theory for the exponents $\chi(\mu)$ and $\chi_1(\mu)$ which describe the dependence of the island and monomer densities at fixed coverage on deposition rate $F$. In addition, the exponents do not depend on whether or not monomers remain superdiffusive or are thermalized (e.g. undergo regular diffusion) after detaching from a dimer. However, we also find that, as was previously found in the case of irreversible growth, the exponent $\chi$ only approaches its asymptotic value logarithmically with increasing $1/F$. This result has important implications for the interpretation of experiments. Good agreement with the RE theory is also found in the case of subdiffusion for point-islands. However, in the case of ramified islands with subdiffusion and $i = 2$, the exponents are significantly higher than predicted due to the fact that monomer capture dominates in the nucleation regime. A modified RE theory which takes this into account is presented, and excellent agreement is found with our simulations.



## 1. Introduction

Recently, there has been significant interest in the effects of anomalous monomer diffusion [1–17] on submonolayer island growth [18–23]. This interest has been partially stimulated by recent experiments [19–21] in which values of the exponent $\chi$ which describes the dependence of the peak island density $N_{pk}$ on the (per site) monomer deposition rate $F$ (e.g. $N_{pk} \sim F^{\chi}$) were obtained which were significantly larger than 1. This result is in contrast to the standard rate-equation (RE) theory prediction [24,25] that in the case of deposition on a 2D substrate with ordinary monomer diffusion (and assuming the existence of a critical cluster size $i$ such that clusters larger than $i$ are stable while clusters of size $i$ and below are unstable) one has $\chi = i/(i + 2)$.

While this result applies in the case of ordinary diffusion such that the dependence of the mean-square monomer displacement on time $t$ satisfies $\langle r^2(t)\rangle \sim t^{\mu}$ with $\mu = 1$, it does not apply in the case of anomalous diffusion. In particular, in Ref. [20] it was suggested that the large value of the exponent $\chi$ found in the case of submonolayer growth of para-hexaphenyl [19] on amorphous mica may be explained by the existence of transient hyperthermal behavior which leads to ballistic monomer diffusion ($\mu = 2$). Similar results, e.g. $\chi > 1$, have also been obtained in the case of submonolayer growth of pentacene on amorphous mica [21]. In addition, in Ref. [22] a RE approach was used to show that for the case of compact islands on a 2D substrate, ballistic diffusion implies that $\chi = 2i/(i + 3)$. We note that transient hyperthermal behavior has also been recently observed in the deposition of Pd/MgO [14] as well as in experiments on pulsed laser deposition [10,17]. In contrast, anomalous diffusion with $\mu < 1$ has been predicted to occur in the case of diffusion on disordered surfaces [1,12] as well as in biological systems [15,16] and has also been observed experimentally in the diffusion of colloidal nanoparticles on a surface [13].

Motivated by this work, one of us has recently developed a RE theory [23] which leads to general expressions for the exponent $\chi$ as a function of the critical island size $i$, substrate dimension $d$, island fractal dimension $d_f$, and diffusion exponent $\mu$, where $0 \le \mu \le 2$. Here the island fractal dimension is defined by the relation $r \sim S^{1/d_f}$ where $r$ is

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the radius of an island and $S$ is the size (number of monomers) in an island. General expressions were also obtained [23] for the dependence of the exponent $\chi_1$, which describes the dependence of the monomer density $N_1$ on deposition rate $F$ at fixed coverage $\theta$ (e.g. $N_1(\theta; F) \sim F^{\chi_1}$ where $\theta$ corresponds to the fraction of the substrate which is covered by monomers and/or islands) in the aggregation regime on $i$, $d$, $d_f$, and $\mu$. Expressions were also obtained for the exponents $\chi'$ and $\chi_1'$ which describe the deposition-rate dependence of the island and monomer densities at fixed dose $\phi = Ft$ ($N(\phi; F) \sim F^{\chi'}$ and $N_1(\phi; F) \sim F^{\chi_1'}$) where $\phi$ corresponds to the number of atoms deposited per adsorption site. As part of this work, two distinct cases were identified - one corresponding to $\mu < \mu_c$ and the other corresponding to $\mu > \mu_c$ - where $\mu_c = 2/d$ for finite $d_f$ or for point-islands with $d \leq 2$ and $\mu_c = 1$ otherwise.

The results obtained in Ref. [23] were based on the assumption that $N_1 \ll N$ in the aggregation regime along with the assumption that for $i > 1$ the Walton relation [26] $N_i \sim N_1^i$ (where $N_i$ is the density of islands of size $i$) holds for anomalous diffusion. In addition, while excellent agreement was found [23] between simulations and the RE theory for the case of irreversible growth ($i = 1$), simulations were not carried out for the case $i > 1$. This case is of particular interest since many experiments, including those discussed in Refs. [19–21], are also believed to correspond to a critical island-size which is significantly larger than 1. In addition, we note that in the case of superdiffusion ($\mu > 1$) with $i > 1$ two distinct physical situations may occur - one in which monomers which detach from islands also travel superdiffusively [7,11], and another in which they are thermalized and undergo normal diffusion. It is also of interest to know if the Walton relation will hold in both of these cases and whether or not they correspond to different scaling behaviors.

Motivated by these considerations, here we present the results of simulations of reversible submonolayer island growth with $i = d = 2$ for both ramified ($d_f \simeq 2$) and point ($d_f = \infty$) islands which were carried out for both the case of subdiffusion ($\mu < 1$) and superdiffusion ($\mu > 1$). In the case of superdiffusion, excellent agreement is obtained with the RE theory predictions of Ref. [23] for both ramified islands and point-islands. We also find that in this case the scaling behavior does not depend on whether or not detached monomers are thermalized or remain superdiffusive. Similarly, good agreement with the RE theory predictions of Ref. [23] is also found in the case of subdiffusion for point-islands ($d_f = \infty$). These results indicate that the Walton relation, along with the scaling arguments used in Ref. [23], both apply in these cases. However, in the case of ramified islands with subdiffusion with $i = 2$, the RE assumption that $N_1 \ll N$ in the dominant portion of the nucleation regime turns out not to hold. As a result, monomer capture dominates while the nucleation regime extends to a coverage which is relatively independent of the deposition rate. A modified RE theory which takes this into account is presented, and excellent agreement is found with our simulations.

This paper is organized as follows. In Section 2 we first review the RE theory, while in Section 3 we discuss the details of our simulations. We then present our simulation results in Section 4 and compare with the corresponding RE theory predictions. Finally, in Section 5, we present our conclusions and discuss possible future work.

## 2. Rate-equation theory

Before discussing our simulations in detail we first briefly review the RE theory discussed in Ref. [23]. In particular, assuming that only monomers are mobile as well as the existence of a critical island-size $i$, in the pre-coalescence regime one may write the following set of contracted REs for the evolution of the monomer density $N_1$ and stable island density $N$ (where $N = \sum_{i+1}^{\infty} N_s$ and $N_s$ is the density of islands of size $s$, where $s$ is the number of monomers in an island),

$$\frac{dN_1}{d\phi} = C_\theta - 2R\sigma_1 N_1^2 - RN_1\sigma_{av}N \tag{1}$$

$$\frac{dN}{d\phi} = \theta^{1-d_f/d} N^{d_f/d-1} \times \left(\frac{dN}{d\theta}\right) = RN_1\sigma_i N_i \tag{2}$$

where $\phi = Ft$ is the dose, $F$ is the deposition rate in monolayers (ML) per second and $R = D/F$, where $D$ is the monomer hopping rate. Here the capture numbers $\sigma_s$ correspond to the propensity of an island of size $s$ to capture a diffusing monomer and are defined via the relation $\alpha_s = DN_1N_s\sigma_s$ where $\alpha_s$ is the average monomer capture rate for an island of size $s$. Also, $\sigma_{av} \equiv \frac{1}{N}\sum_{s>i}\sigma_s N_s$ is the average capture number for stable islands, and $C_\theta \simeq 1 - \theta - \sum_{s=2}^{i} N_s(RN_1\sigma_s - \gamma_s)$ where $\gamma_s$ is the (monomer) detachment rate for islands of size $s \leq i$.

Assuming that in the asymptotic limit of large $D/F$, one has $N_s \ll N \ll 1$ for $1 \leq s \leq i$ implies that $C_\theta \simeq 1 - \theta$. Combining this with the steady-state assumption that at late-time $\frac{dN_1}{d\phi} \simeq 0$ implies,

$$N_1 \simeq \frac{1}{RN\sigma_{av}} \tag{3}$$

The exponents $\chi, \chi_1, \chi', \chi_1'$ can then be obtained using Eqs. (2) and (3), along with the Walton relation $N_i \sim N_1^i$, as well as specific assumptions for the scaling of $\sigma_i$ and $\sigma_{av}$ as a function of island-density $N$ as discussed in more detail below.

### 2.1. Case $\mu > \mu_c$

In this case by assuming that the average capture number $\sigma_{av}$ is proportional to a power of the average cluster size, along with scaling arguments it was found [23] that $\sigma_{av}(\phi; N) \sim N^{-\delta/d_f}$ and $\sigma_{av}(\theta; N) \sim N^{-\delta/d}$ where the exponent $\delta$ satisfies,

$$\delta = d - 2/\mu \tag{4}$$

for finite island fractal dimension $d_f$ or for point-islands with $d \leq 2$. This implies the existence of a critical value of $\mu$ ($\mu_c = 2/d$) such that for $\mu = \mu_c$ one has $\delta = 0$ and the standard RE theory (corresponding to ordinary diffusion in $d = 2$) applies, while for $\mu > \mu_c$ ($\mu < \mu_c$) one has $\delta > 0$ ($\delta < 0$) [27]. Using this result along with the Walton relation in Eqs. (2) and (3) leads to the following results [23] for $i = d = 2$,

$$\chi = \frac{4\mu}{6 + \mu d_f}, \quad \chi_1 = \frac{2 + \mu d_f}{6 + \mu d_f} \tag{5}$$

$$\chi' = \frac{\mu d_f}{3 + \mu(2d_f - 3)}, \quad \chi_1' = \frac{1 + \mu(d_f - 1)}{3 + \mu(2d_f - 3)}. \tag{6}$$

As expected, for the case of ramified islands with $d_f = 2$ for which the dose is equal to the coverage, one has $\chi = \chi'$ and $\chi_1 = \chi_1'$. In particular, Eqs. (5) and (6) imply in this case that $\chi = \chi' = 2\mu/(3 + \mu)$ and $\chi_1 = \chi_1' = (1 + \mu)/(3 + \mu)$. In contrast, in the case of point islands ($d_f = \infty$) the exponents $\chi$ and $\chi_1$ are not well-defined since the coverage does not increase and the island-density does not saturate. In this case, one has $\chi' = \chi_1' = 1/2$ in good agreement with the standard RE prediction for $i = 2$ corresponding to ordinary diffusion.

### 2.2. Case $\mu < \mu_c$

In this case it was assumed [23], by analogy with the case of irreversible growth with ordinary diffusion and $d = 1$ [28], that both $\sigma_i$ and $\sigma_{av}$ scale in the same way, e.g. $\sigma_i(\theta; N) \sim \sigma_{av}(\theta; N) \sim N^{-\delta'}$. Such an assumption is also consistent with the fact that in our simulations with $\mu < 1$, which correspond to a continuous time random-walk (CTRW) [5] with a power-law distribution of waiting times $P(\tau') \sim (D_0\tau')^{-1-\mu}$ (see Section 3.1) the subdiffusive behavior is due to a "rescaling of the time" which affects both small and large islands equally. In this case using the REs (2) and (3) (but now with $R = D_0/F$) along with the Walton relation $N_i \sim N_1^i$ leads to the general results,

$$\chi = \frac{i}{i(1 - \delta') + 1 + d_f/d} \;\; ; \;\; \chi_1 = 1 - \chi(1 - \delta') \tag{7}$$

$$\chi' = \frac{i}{i(1 - \delta') + 2} \;\; ; \;\; \chi_1' = 1 - \chi'(1 - \delta') \tag{8}$$