Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information
Electrodeposition model with surface relaxation predicts temperature and current effects in compact and dendritic film morphologies

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S.I Model with other distributions of allowed numbers of hops

S.I.1 Delta distribution

This is the most common case in LM models with long surface diffusion lengths: $P_D(G) = 1$; $P_D(N) = 0$ for $N \neq G$. We studied films produced with collimated cation flux and this distribution.

The film morphology is similar to that produced with the Gaussian distribution, shown in Figs. 2(a)-(d) of the main text. The average numbers N_T and N_D have the same scalings shown in Figs. 4(a) and 4(b), respectively, and the roughness follows the same scaling in time as that of Fig. 3. The roughness evolution also matches that of the CV model with suitable rescaling and confirms that this LM model is in the VLDS class.

However, significant differences are observed in the distributions of numbers of executed hops of individual adatoms, $Q(N_T)$. Fig. S1(a) shows this distribution for $G = 60$ and $P = 0.01$ at $t = 1000$ (the distributions at $t = 10$ and $t = 100$ are quite similar). There is a sharp peak at $N_T = G$, which means that it is much more probable for an adatom to execute G hops than to execute $G - 1$ hops or $G + 1$ hops. The case $N_T = G$ generally corresponds to adatom motion on a terrace, whereas $N_T = G + 1$ usually requires detachment events and $N_T = G - 1$ is usually a case of encountering a terrace border after $G - 1$ hops. The peak of $Q(N_T)$ is an artifact of the model, which is hardly expected in a physical system. It contrasts with the continuous shape of $Q(N_T)$ for the Gaussian hop number distribution $P_G(N)$, as shown in Fig. S1(a).

S.I.2 Exponential Distribution

Here we consider a discretization of the exponentially decreasing distribution $P_E(N) = \exp(-N/G)/G$ and deposition with collimated flux.

For the same growth parameters G and P, the roughness of the films is smaller than that of the films produced with the other distributions (Gaussian and delta). However, the terrace borders are apparently more disordered than in the previous cases.

Fig. S1(b) shows the scaled distribution of the total numbers of hops of individual adatoms, $Q(n_T)$, for $G = 60$ and $P = 0.01$, at $t = 1000$. The stretched exponential form with the variable $(n_T/N_T)^{0.7}$ is similar to that of the CV model at low temperatures [1], in

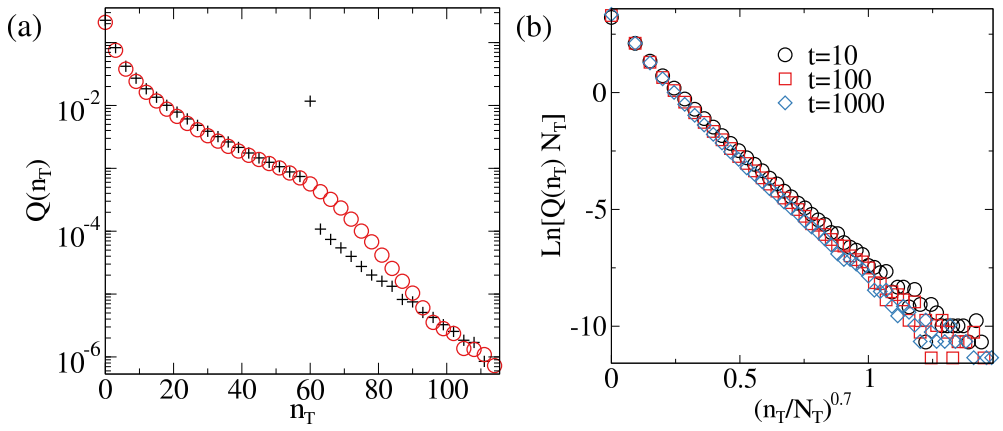

Figure S1: Distributions of numbers of executed hops of the LM model with $G = 60$ and $P = 0.01$: (a) delta distribution (+) and Gaussian distribution (circles) of hop numbers at $t = 1000$; (b) the exponentially decreasing distribution of hop numbers at three times.

which aggregation to lateral NNs is effectively irreversible. This occurs because there is a high probability that $N \ll G$ is chosen from the exponential hop number distribution; the most probable choices are $N = 0$ and $N = 1$. Even if GP is relatively large (e.g. films with $GP \sim 10$ were simulated), it is highly probable that the chosen value of N gives $NP < 1$; if so, the adatom will probably not move if it has a lateral NN or will move a short distance on a terrace. This also explains the disordered terrace borders observed in the film surfaces. The average numbers of executed hops and detachments, N_T and N_D, also show simple scaling relations with G and P, with GP being the main scaling variable, but no change in those relations is observed for $GP > 1$.

From the analysis of the three distributions of allowed numbers of hops, we understand that the Gaussian distribution is a physically reasonable choice. In recent simulations of submonolayer deposition with LM models, the advantage of using this type of hop number distribution was also highlighted [2].

S.II Details of the simulations

S.II.1 Model of electrodeposition of compact films (collimated flux)

This model was simulated in lattices with lateral size $L = 1024$. The maximal growth times correspond to the deposition of 10^4 atomic layers (i.e. maximal average height $\overline{h} = 10^4$). The model parameters were in the ranges $10 \leq G \leq 280$ and $0.001 \leq P \leq 0.1$. Comparison with some simulations in size $L = 2048$ showed no finite-size effect. The average quantities were calculated from 100 configurations produced with each parameter set.

Simulations of this model ran in workstations with AMD Ryzen Threadripper 2970WX processors, where a single configuration with $G = 280$ and $P = 0.008$ was grown in ~ 7 hours. The computation time rapidly increases with G, especially for the largest P, in which frequent resetting of the number of allowed hops occurs.

S.II.2 CV model

The CV model of vapor deposition was simulated in lattices with lateral size $L = 1024$ for $10 \leq R \leq 10^5$ and $0 \leq \epsilon \leq 0.1$. The maximal number of deposited layers was 10^4. No finite-size effect was observed. Average quantities were obtained from 100 independent realizations for each parameter set.

Simulations of this model ran in workstations with AMD Ryzen Threadripper 2970WX processors. For $R = 10^5$ and $\epsilon = 0.01$, each configuration was grown in ~ 22 hours. This parameter set provides approximately the same roughness evolution as the electrodeposition model with $G = 280$ and $P = 0.008$.

In the ranges of parameters of our simulations, the model of electrodeposition of compact films runs four times faster than the CV model. However, this comparison of execution times may change for much larger values of R and G. In the CV model, that time increases linearly with R [3]. In the electrodeposition model, that time typically increases linearly with the number of executed hops, $\langle N_T \rangle$, which in turn increases faster than linearly with G, as shown in Fig. 4(a) of the main text. It is also important to recall that the two models are designed for different applications, so we cannot anticipate computational difficulties in applying the electrodeposition model based on comparisons with the (widely studied) CV model.

S.II.3 Model of electrodeposition of dendritic films (diffusive flux)

The model of electrodeposition of dendritic films (diffusive cation flux) was simulated in lattices with lateral size $L = 512$. Again, some tests in lattices with $L = 1024$ did not show significant finite-size effects. The simulated model parameters were $10 \leq G \leq 280$, and $0 \leq P \leq 0.1$. Average quantities were obtained from 100 realizations. In all runs, the deposition stopped when the maximal height of the deposit reached $h_{max} = 10^3$.

In the longest runs, for $G = 280$ and $P = 0.001$, the deposited mass corresponded to a number of monolayers ≈ 240 and average height ≈ 750 [a porous deposit, as indicated by the top view in Fig. 8(b) of the main text]. The corresponding execution time was ~ 5 hours in a Xeon Silver 4110 processor.

References

[1] E. E. Mozo Luis, I. S. S. Carrasco, T. A. de Assis, and F. D. A. Aarão Reis. Statistics of adatom diffusion in a model of thin film growth. Phys. Rev. E, 102:012805, 2020.

[2] T. Martynec and Sabine H. L. Klapp. Modeling of nonequilibrium surface growth by a limited-mobility model with distributed diffusion length. Phys. Rev. E, 100:033307, 2019.

[3] I. S. S. Carrasco and T. J. Oliveira. Height fluctuations in homoepitaxial thin film growth: A numerical study. Phys. Rev. Res., 2:013385, 2020.