

Lattice gas study of thin-film growth scenarios and transitions between them: Role of substrateE. Empting ^{*}, M. Klopotek, A. Hinderhofer, F. Schreiber , and M. Oettel *Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen, Germany* (Received 8 October 2020; revised 21 December 2020; accepted 17 January 2021; published 8 February 2021)

Thin-film growth is investigated in two types of lattice gas models where substrate and film particles are different, expressed by unequal interaction energy parameters. The first is of solid-on-solid type, whereas the second additionally incorporates desorption, diffusion in the gas phase above the film and readsorption at the film (appropriate for growth in colloidal systems). In both models, the difference between particle-substrate and particle-particle interactions plays a central role for the evolution of the film morphology at intermediate times. The models exhibit a dynamic layering transition which occurs at generally lower substrate attraction strengths than the equilibrium layering transition. A second, flattening transition is found where initial island growth transforms to layer-by-layer growth at intermediate deposition times. Combined with the known roughening behavior in such models for very large deposition times, we present four global growth scenarios, charting out the possible types of roughness evolution.

DOI: [10.1103/PhysRevE.103.023302](https://doi.org/10.1103/PhysRevE.103.023302)**I. INTRODUCTION**

The evolution of structure in thin-film growth is a topic of broad interest, both from the perspective of nonequilibrium statistical mechanics as well as from an applied point of view where certain properties such as, e.g., a smooth film with minimal roughness may be desirable. For homoepitaxial growth, quantitative and detailed insight has been reached [1]. For growth of a substance on a substrate consisting of a different material the phenomenology is broader. If both the substrate and the film material are crystalline with different equilibrium lattice parameters, then one speaks of genuine heteroepitaxial growth. However, substrate or film may be amorphous in which case heteroepitaxial effects (such as residual stresses) are absent, but effects of different surface energies are still present. The experimental systems of interest encompass metal or semiconductor growth (which is in most cases heteroepitaxial and in which the film particles can be considered as isotropic) [2] as well as the growth of organic semiconductors on varying substrates where the film molecules are mostly anisotropic [3,4]. For organic semiconductor growth, genuine heteroepitaxy may occur (e.g., for growth of Pentacene on C60 crystal layers) but, on the other hand, may also be absent (e.g., when using amorphous silica substrates, which are of enormous practical importance and probably the most popular material).

Typically, one distinguishes between layer-by-layer (LBL) growth, Vollmer-Weber or island (ISL) growth and Stranski-Krastanov (SK) growth which is characterized by initial LBL growth changing to ISL growth [5]. The latter is often characterized as a transition from two-dimensional (2D) growth to 3D growth (see Ref. [6] for an early experimental and simulation study with organic molecules). These growth modes

can be distinguished using the film roughness σ [root-mean-square (rms) deviation from the average film height \bar{h}] as an observable, which is easily accessible in both experiment and simulations. LBL growth is characterized by oscillations in $\sigma(\bar{h})$, and ISL growth is reflected in a quick rise in $\sigma(\bar{h})$, stronger than in statistical (Poisson) growth [$\sigma(\bar{h}) \propto \bar{h}^{1/2}$]. SK growth shows initial roughness oscillations, which subsequently change to a monotonic rise of σ with \bar{h} . The latter may be described with a power law, $\sigma(\bar{h}) \propto \bar{h}^\beta$ where β is the roughening exponent [7].

In explaining the occurrence of LBL vs. ISL growth or near-equilibrium conditions, it is common practice to invoke equilibrium surface free energies (interface tensions), in particular the ratio $r = (\gamma_{sv} - \gamma_{sf})/\gamma$. Here, γ is the interface tension between film and vapor, γ_{sv} the one between substrate and vapor and γ_{sf} the one between substrate and film (see, e.g., Ref. [8]). The vapor usually has a very low density and corresponds to the vacuum in typical deposition experiments. If $r = 1$, then equilibrium wetting occurs (the free energy is lowest when a thick film is inserted between substrate and vapor), which is understood as the condition for LBL growth. If $|r| < 1$, then partial wetting occurs with droplets of film material appearing, whose contact angle $\theta_Y = \arccos(r)$ varies between 0° and 180° . This is understood as a condition for ISL growth. (The case $r = -1$ is not relevant to film growth as it refers to equilibrium drying, the formation of a thick film of vapor between substrate and film material.) By the use of surface free energies, this argument for the distinction between LBL and ISL growth is an equilibrium one. However, in a real system kinetics will enter the picture, and may invalidate the use of equilibrium arguments. We will address this point by studying growth in a simple lattice model where the equilibrium properties are known and can be used to gauge the results for growth.

Computational studies of film growth generally invoke one of two widely used simulation methods: kinetic Monte Carlo

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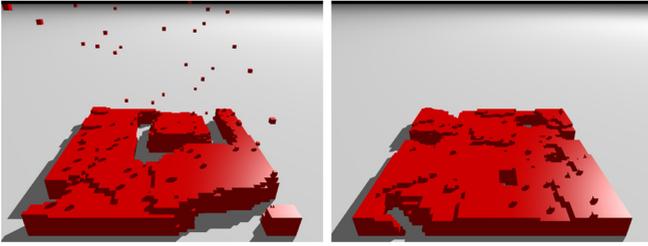


FIG. 1. Snapshots of the system at $\epsilon = -3$, $\epsilon_{\text{sub}} = -1.33$, $\Gamma = 10^4$ after deposition of 5 MLs in the CGM (left) and the SOS model (right). Since particle moves are not restricted in the CGM, we can see in the CGM snapshot (i) the formation of a gas phase above the film and (ii) more pronounced partial wetting of the substrate

(KMC) and molecular dynamics (MD). KMC simulations can be lattice-based or off-lattice [9] and are characterized by local, discrete “moves” of particles with no explicit memory of past ones. Each “move” occurs at a rate that adheres to the instantaneous energy (barrier) encountered at the current configuration. The simplicity of especially lattice-based KMC simulations allows to study large systems and thick films [10,11]. On the other hand, MD simulations of growth incorporate the full particle dynamics, but studying multilayer growth for reasonably large systems is only practically possible for isotropic particles (see, e.g., Refs. [12,13]). All-atom simulations of organic semiconductor growth can model faithfully the growth process of a specific molecule. Examples are Pentacene (PEN) growth on C_{60} (Refs. [14,15]), reversely the C_{60} growth on PEN [16] or silica [17] and 6T monolayer growth on SiO_x (Ref. [18]). These models are, however, generically limited by the small number of particles for computational reasons. Therefore, lattice-based KMC simulations are more suited to study the multilayer regime and to explore the parameter space more thoroughly.

In this paper, we investigate dynamic transitions between different growth modes using KMC simulations. We both quantify these transitions as well as map out the conditions under which they occur. We adopt the well-known lattice gas model for particles with nearest-neighbor interactions living on a simple cubic (SC) lattice. Particles at the substrate and in the film are treated differently by means of their interaction energies, i.e., the interaction strength between two film particles is different from the interaction strength between a film and a substrate particle. However, in our modeling genuine heteroepitaxy is absent since the lattices of the substrate and the film are assumed to be equivalent. The modeling should thus actually correspond nicely to the growth on amorphous substrates such as the very commonly used oxidized silica wafers. Both a solid-on-solid (SOS) model and a second, more general model are investigated. Within both, deposition of particles and diffusion occurs at the film surface. However, in the second model, arbitrary desorption and readsorption of particles can occur, along with diffusion in a gas phase hovering above the film (in Fig. 1 we show snapshots of thin films comparing both models). The CGM is less restrictive in local transport than the SOS counterpart (its catalog of possible local “moves” is broader), and is novel (to our knowledge) in the KMC literature for thin-film growth. We call this version of the model the colloidal growth model (CGM) since

it is describing a typical setup for the growth of colloidal crystalline films. Colloidal particles are immersed in a solvent, generally rendering their bulk and surface dynamics purely diffusive. Inspired by sedimentation-diffusion [19], deposition on top of a substrate proceeds by drift diffusion.

As a main result, we identify two dynamic transitions in both models: (i) between ISL and LBL growth (“dynamic layering transition”) via a novel order parameter that quantifies the difference in coverages of the first and second layers and (ii) a “flattening transition” of the ISL growth mode back to (near-)LBL growth at intermediate times—after a total deposition of a few monolayers—the onset of which can be shown to be the moment the first layer becomes completely filled. The possible occurrence of these transitions gives rise to certain global growth scenarios (characterized by the roughness evolution with time) when observing the film evolution over long deposition timescales.

The paper is structured as follows: Section II introduces lattice-based KMC simulations, in particular the two variants studied here. In Sec. III the two dynamic transitions mentioned above are characterized, and additionally the global growth scenarios are discussed. In Sec. IV we relate our observations to existing experimental results for thin-film growth, and in Sec. V we provide some conclusions and an outlook.

II. KMC LATTICE SIMULATIONS

A. General considerations

KMC SOS lattice models have a venerable history in the study of film growth [1]. In the easiest realization on a cubic lattice, each particle must be supported, i.e., has a particle or substrate below it (no overhangs) and particles are not allowed to be located in the vapor phase (in some models, particles are allowed to desorb from the film, but are then consequently removed from the simulation [20]). This leads to films that exclude vacancies and overhangs and imposes an imminent vacuum above the film. In many experimental scenarios, this is a reasonable approximation, since desorption is often negligible.

In the simplest realization of this model (stochastic growth), new particles are deposited at random sites on top of the growing film and stick there without diffusing any further [21]. In this model, the film grows in a stochastic manner driven by the deposition process only, and its roughness will behave as $\sigma \propto \Theta^\beta$ with $\beta = 1/2$, where Θ is the number of deposited monolayers (MLs) and

$$\sigma = \sqrt{\frac{1}{N} \sum_{i=1}^N (h_i - \bar{h})^2} \quad (1)$$

is the rms of the deviation from the mean height, with h_i being the film height (in lattice units) at lattice site with label i and \bar{h} the mean film height.

Surface diffusion can be incorporated into the simulation in the following most intuitive way: During each time step either a new particle is inserted at a random site with probability f or an existing particle is moved to a neighboring site with probability $1 - f$ (Refs. [22,23]). Here it is crucial how one handles interlayer diffusion: If it is forbidden, then

particles will always remain in the layer into which they were deposited, and the roughness will show the same $\sigma \propto \Theta^{1/2}$ behavior seen in the stochastic growth models. If interlayer transport is allowed, then it can occur either at the same rate as diffusion within a layer, or one can assign an energy cost to this layer change (the so-called step edge or Ehrlich-Schwöbel barrier). Mound formation in epitaxial growth with an ensuing roughening exponent $\beta \neq 1/2$ is strong evidence for the effects of such a barrier, see Refs. [7,21] for an overview.

This simple model has been modified in various ways over the years. One early modification of the stochastic growth model was the Wolf-Villain model [24,25]. Here particles will diffuse immediately after deposition before becoming immobilized forever. More recently, the quantitative accuracy of the SOS model has been improved by implementing fluctuating interparticle attractions [26]. Other modifications include a first-passage time approach [27] (which can lead to a significant acceleration of simulations), and the introduction of anisotropic interactions [28].

In other lattices, e.g., face centered cubic, one finds additional effects: Since each particle now needs multiple occupied sites in the layer below to be supported, one has to consider what happens if not all supporting sites are occupied. A frequently invoked mechanism is downward funneling [29], where particles will “fall” into lower layers until they have reached a fully supported position. This leads to films growing in a much smoother fashion than in an SC lattice but is also a strong simplification of the processes occurring during film growth [1]. A somewhat more sophisticated approach is to modify this downward-funneling behavior by trapping new particles at the sides of protrusions, leading to overhangs and consequently voids inside the film [30].

A number of studies addressed the evolution of 3D structure in homoepitaxial growth, see, e.g., [10,31] for recent examples with large substrates and rather thick films. Previous KMC works on genuine heteroepitaxial growth focused on the problem of SK growth by incorporating strain and stress release [32–34], or on simulating the behavior of specific systems (e.g., C60 on Pentacene [16]) by fitting the corresponding KMC parameters from atomistic calculations.

B. Solid-on-solid model

The simulation is divided into discrete but variable time steps, which are Poisson distributed. During each of these time steps exactly one event occurs [35,36]. Such events can be, e.g., particle moves or insertions. Each event occurs with an average rate k_i , which is a parameter specified *a priori*. In general, KMC being event-driven means that the algorithm is “rejection-free,” since one tracks all events that are possible in each step and then chooses one of these events. Our simulations entail attractive interactions between neighboring particles ϵ and particles on top of the substrate ϵ_{sub} . All energies are given in units of the thermal energy $k_B T$. These affect the rates at which events occur depending on the local environments of the respective particles. We realize this by introducing a Metropolis step, accepting each move with a probability $p = \min(1, \exp(-\Delta E))$ depending on the change in internal energy this move would cause. Hence our algorithm is “rejection-free” regarding steric repulsions only.

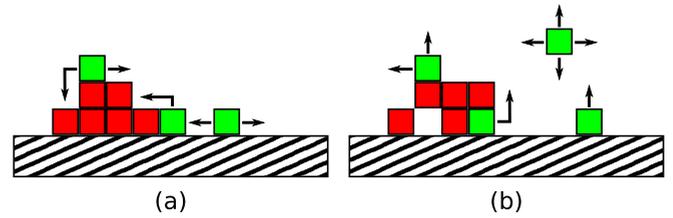


FIG. 2. Schematic 2D drawings showing (a) the diffusion moves which are allowed in the SOS model (note that neither overhangs nor desorptions are possible) and (b) additional moves which are allowed in the CGM.

While this of course leads to some moves being rejected, this hybrid method [37] significantly reduces the overhead of keeping track of state changes. After each move attempt, we then increase the time by a random $\Delta t = -\ln(r)/k_{\text{tot}}$ where $k_{\text{tot}} = \sum_i k_i$ is the total rate of possible events at the current state and $r \in (0, 1]$ is a random, uniform number. The average length of these time steps is $1/k_{\text{tot}}$. This procedure leads to more accurate dynamics (incorporating more fluctuations) than using a fixed-length time step of length $1/k_{\text{tot}}$ (Ref. [38]).

In the SOS version, we consider insertion moves at random lateral positions (x, y) on top of the growing film with rate $k_{\text{ins}} = F$, diffusion moves to lateral next-neighbor positions with $\Delta z = 0$, where z is the vertical coordinate, with rate k_{hop} , and layer-changing moves to lateral next-neighbor positions with $\Delta z = \pm 1$ with rate $k_{\text{ES}} = k_{\text{hop}} \exp(-E_{\text{ES}})$ where E_{ES} is the (dimensionless) Ehrlich-Schwöbel barrier, which effectively leads to a rescaling of the acceptance probability p to $p = \min(1, \exp(-\Delta E)) \exp(-E_{\text{ES}})$. We chose this implementation in order to ensure that detailed balance is obeyed. All these moves have to respect the SOS condition of no vacancies or overhangs in the film; see Fig. 2(a) for a sketch of all possible diffusion moves.

The 2D diffusion constant (in lattice units) of a free film particle on top of the substrate or on top of a completely filled layer is simply $D = k_{\text{hop}}$. Thus, the four parameters of the model are $\Gamma = D/F$ and the energies ϵ , ϵ_{sub} , E_{ES} . To provide an experimental context [39,40], note that, e.g., for room temperature growth of C60 on C60 one may estimate diffusion coefficients $D = O(10^8) \text{ nm}^2/\text{s}$, and with fluxes $F = 0.001 \dots 0.1 \text{ monolayers/s}$ one finds $\Gamma = O(10^9) \dots O(10^{11})$ (lattice units) $^{-4}$ where a real C60 lattice unit is approximately 1 nm. Furthermore, using the Girifalco potential [41], one can estimate the interaction between two neighboring C60 particles at room temperature as $\epsilon \approx -10$ in units of $k_B T$, where k_B is the Boltzmann constant and T is the (room) temperature. At this point we can remark that simulating such high values of Γ and $|\epsilon|$ is challenging, see Ref. [42] for a recent, state-of-the-art example examining few layer growth with C60. We will return to this problem below.

C. Colloidal growth model

In the second version of the model, we relax the restriction on the next-neighboring site diffusion moves. Any such move is now allowed if it is not blocked by another particle or the substrate. In addition to the moves allowed in the SOS model, this allows for desorption from the film, diffusion in the vapor

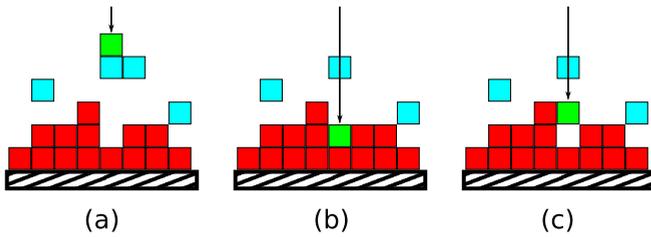


FIG. 3. Different methods of inserting new particles into the simulation box in the CGM. Red particles are part of the film, blue particles are not, and the green particle is the newly inserted particle. (a) The newly inserted particle diffuses downwards until it touches any other particle (including particles in the gas). This leads to the formation of large clusters in the gas phase. (b) The new particle is inserted on the topmost film particle at the chosen lateral position. (c) The new particle is inserted at the topmost position with a film particle at a neighboring site (if that height is larger than the position of the topmost film particle). This is most similar to colloidal deposition.

phase and readsorption at the film. Therefore, the growing film is covered by a dynamically changing gas “cloud” and new particles are incorporated into the film through possibly direct deposition and also adsorption from this gas layer. A layer-changing particle move still requires a support particle around which the particle moves up or jumps down one layer. See Fig. 2(b) for a sketch of all possible diffusion and evaporation moves in the CGM.

The insertion move now requires more discussion. In general, the film contains cavities and there is an adjacent gas phase with freely floating particles. Thus there are several sensible ways to insert new particles into the system, depicted in Fig. 3. One natural implementation would be to insert particles at the top of the box and letting them sediment downwards until they meet any other particle [Fig. 3(a)]. However, this leads to the formation of large clusters inside the gas phase which do not dissolve during the simulation and consequently block most new particles from ever reaching the substrate or film. Since we have not implemented cluster moves, the clusters themselves are stationary and thus the blockage for newly deposited particles persists and leads to unphysical growth behavior.

More similar to insertion in the SOS model, we first define as “film” the set of particles which are connected via next neighbors to the substrate. We can choose a random position of the substrate and insert a new particle on top of the highest particle there which is part of the growing film (i.e., not in the gas phase [Fig. 3(b)]). Last, and closer in spirit to colloidal growth, we relax this SOS like condition insofar, as particles can also get “caught” at a certain height by neighboring particles which belong to the growing film, leading to the formation of overhangs [Fig. 3(c)]. We choose this insertion method for all results shown below. All in all, this model is similar in spirit to colloidal deposition experiments in solution [43], hence we call this model a CGM.

The definition and calculation of the rates is unchanged compared to the SOS model. The particles can desorb into the gas phase with an attempt rate D . The dynamics in the gas are modeled by nearest-neighbor hops with rate D . The CGM

obeys detailed balance (including with the gas) completely if the explicit insertion event is turned off. We remark that the difference between the CGM and the SOS model lies in the catalog of allowed particle moves. Sometimes, a difference between atomistic and colloidal growth is discussed with respect to the differing interaction range in atomic or molecular systems and colloidal systems, see, e.g., Ref. [44].

We note that the CGM is a very generic extension of the SOS model without unphysical restrictions but it leads to a substantial amount of simulation time being spent on simulating diffusion moves inside the vapor, of particle desorption and readsorption, and necessitates more bookkeeping. However, in contrast to SOS models, there is a well-defined equilibrium limit for the CG, since the whole phase space can be explored.

Most of the results in the CGM will be for a box size $L \times L \times L_z$ with $L = 64$ and $L_z = 200$. The upper boundary of the box is a hard wall, while the lower boundary is the attractive substrate. For the SOS model, only the lateral extension is important, here we use $L = 32 \dots 300$. The main computational observable is the roughness σ [defined in Eq. (1)] as a function of time. The time is proportional to the amount of deposited material (total coverage) Θ (in units of filled monolayers). We will also employ the layer coverage $\Psi_i = N_i/L^2$, where N_i is the number of particles in layer i . The rather moderate lateral system sizes are sufficient for studying the roughness behavior, as evidenced by the results below.

As an example for configurations occurring in growth, in Fig. 1 we show a comparison of snapshots from the CGM and the SOS model for parameters corresponding to initial island growth. The relaxed restrictions on diffusion moves in the CGM compared to the SOS model lead to a more pronounced formation of islands.

III. RESULTS

As we noted earlier, simulations using realistic values for Γ and ϵ fitting actual growth experiments are numerically challenging. Nevertheless we conjecture that results from calculations at lower Γ , $|\epsilon|$ can be extrapolated to larger values using the following scaling arguments.

For homoepitaxial submonolayer growth, such a scaling relation can be derived. In a one-component system, it has been shown [21] that the island density in the submonolayer at low densities scales with

$$n \propto \frac{\exp\left[-\frac{\epsilon_0}{k_B T(i^*+2)}\right]}{\Gamma^{i^*/(i^*+2)}}, \quad (2)$$

where ϵ_0 (with proper energy units) is the interaction strength between nearest neighbors and $i^* + 1$ is the size of the smallest stable cluster. If we now assume that $i^* = 1$ (i.e., that dimers are stable, corresponding to large $|\epsilon_0|$), the island density is constant if:

$$\frac{|\epsilon_0|}{k_B T} - \log \Gamma = \text{const}, \quad (3)$$

i.e., a simulation with a $\Gamma < \Gamma'$ would yield the same results as one with Γ' , as long as one would use an appropriately scaled $|\epsilon_0| < |\epsilon'_0|$. For the example above (C60 growth), island densities at the physical values $\epsilon'_0 \approx -10 k_B T$ and $\Gamma' \approx 10^9$

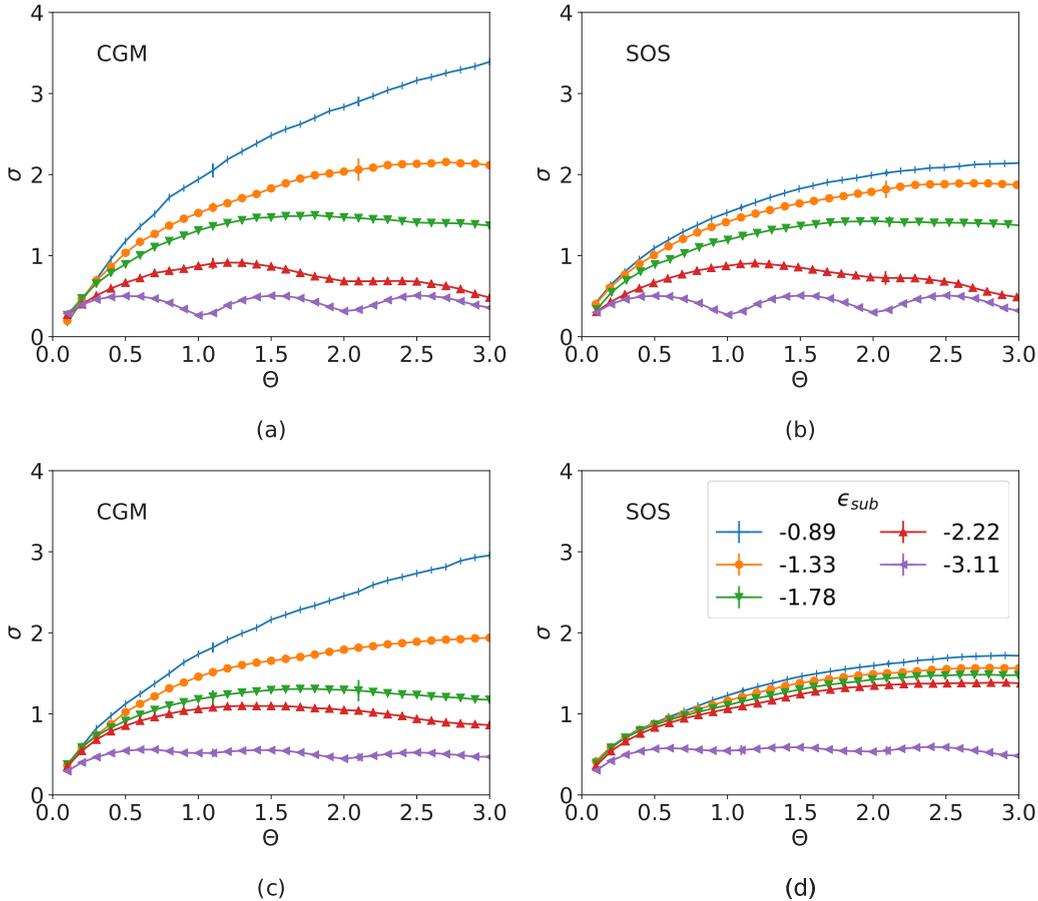


FIG. 4. Evolution of roughness in the CGM and the SOS model for $\Gamma = 10^4$ and different substrate strengths ϵ_{sub} , averaged over five runs. (a) $\epsilon = -3$, CGM; (b) $\epsilon = -3$, SOS; (c) $\epsilon = -5$, CGM; (d) $\epsilon = -5$, SOS. The legend in (d) also applies to (a)–(c). Vertical lines indicate statistical errors, deduced from five independent runs for each parameter set.

should correspond to island densities at $\epsilon \approx -3 k_B T$ and $\Gamma \approx 10^6$.

For the more general case considered here, we are treating multilayer growth, and the two additional energy parameters (ϵ_{sub} , E_{ES}) presumably enter a possible scaling relation. However, except for film-roughness scaling in the epitaxial case with no ES barrier (see below), scaling relations have not yet been identified for multilayer growth.

In Sec. III A and III B below, we consider a vanishing ES barrier $E_{\text{ES}} = 0$.

A. Dynamic layering transition

In Fig. 4 we show the roughness evolution up to a total coverage $\theta = 3$ both for the SOS model and the CGM, for $\epsilon = -3$ and -5 , respectively, each for a range of substrate attractions ϵ_{sub} . We found that in the CGM and for very weak particle-substrate interactions $|\epsilon_{\text{sub}}| \lesssim 0.8$, the initially deposited particles will form floating clusters which then coalesce into a film which might or might not be connected to the substrate, which yields strongly varying results for σ . Hence we only consider values of $|\epsilon_{\text{sub}}| \gtrsim 0.9$. For both models it is seen that on increasing the magnitude of ϵ_{sub} , the system will go from an evolution with increasing roughness to an evolution with oscillating roughness, which indicates a

transition from islands forming on top of the substrate to LBL growth. This transition (abbreviated as ISL \leftrightarrow LBL) can be considered as a dynamic layering transition.

Layering transitions can also be found in *equilibrium* systems as a particular form of a wetting transition. It is useful to recall the equilibrium wetting and layering behavior of the lattice gas model before discussing further the dynamic layering transition. Wetting transitions are conveniently discussed in a diagram with temperature and the reduced substrate attraction strength $\Upsilon = \epsilon_{\text{sub}}/\epsilon$ as axes. For the lattice gas, here we use a ϵ - Υ diagram which corresponds to a $1/T$ - Υ representation. Wetting transitions can only occur for particle-particle interaction strengths $|\epsilon| > |\epsilon_c|$ where $\epsilon_c \approx -0.89$ is the bulk critical attraction strength for the gas-liquid separation. Here, we interpret the high-density liquid phase as the condensed (solid) phase in the growing film. One studies the system at the substrate at coexistence conditions such that far away the system is in the gas phase. The equilibrium net adsorption at the substrate displays a characteristic behavior near a critical reduced strength $\Upsilon_c(\epsilon)$: It may diverge continuously to infinity as $\Upsilon \rightarrow \Upsilon_c$ (critical wetting), it may jump discontinuously to infinity (first order wetting), or it may jump discontinuously to a value corresponding to a net coverage of n layers (n th layering transition). The lattice gas model as used here is equivalent to the Ising model on a few

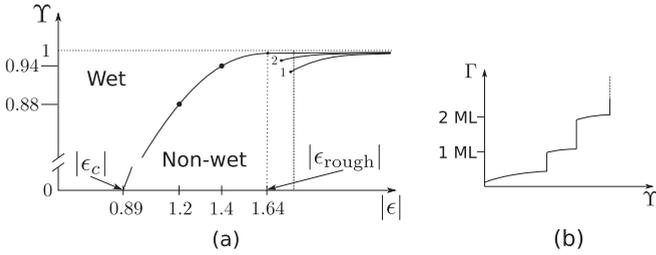


FIG. 5. (a) Schematic equilibrium wetting phase diagram for the lattice model in 3D for $\Upsilon \equiv \epsilon_{\text{sub}}/\epsilon$ vs. $|\epsilon|$. The critical point for liquid-vapor phase separation is at $|\epsilon| = \epsilon_c$. The curve originating at $|\epsilon_c|$ is the line of the wetting transition (thin films of adsorbed liquid at substrates with attraction strength ϵ_{sub} below that line, thick films for ϵ_{sub} above that line). This is second order until $|\epsilon| = \epsilon_{\text{rough}} \approx -1.64$, which denotes the critical attraction strength for roughening. For $|\epsilon| > |\epsilon_{\text{rough}}|$ layering transitions occur (indicated with 1 and 2) where the effective thickness of the adsorbed film jumps to values close to 1 or 2 lattice units. The explicit data points are from simulations [45], for more details and discussion see Ref. [46]. (b) Schematic equilibrium adsorption Γ as function of Υ for the path marked by the blue dashed line in (a).

redefinitions (summarized in Appendix A), its wetting behavior has been studied in Refs. [45,46]. The schematic wetting phase diagram [i.e., the curve $\Upsilon_c(|\epsilon|)$ for wetting transitions] is sketched in Fig. 5(a). A second interaction strength relevant for the wetting transition is the roughening point $\epsilon_{\text{rough}} \approx -1.64$. For $|\epsilon| < |\epsilon_{\text{rough}}|$, steps on the film surface can be created with no free energy cost whereas for $|\epsilon| > |\epsilon_{\text{rough}}|$ the step free energy is finite. The line $\Upsilon_c(|\epsilon|)$ for $|\epsilon_c| < |\epsilon| < |\epsilon_{\text{rough}}|$ describes critical wetting. For $|\epsilon| > |\epsilon_{\text{rough}}|$ layering transitions occur [the lines labeled with 1 and 2 for the first and second layering transition in Fig. 5(a)]. In Fig. 5(b), we show the characteristic behavior of film adsorption on varying the control parameter Υ when it crosses two layering transitions [blue dashed line in Fig. 5(a)]. It is important for the subsequent discussion of the dynamic layering transition that for the high attraction strengths considered there ($|\epsilon| \geq 3$), all equilibrium layering transitions occur very close to $\Upsilon_c = 1$ (which is the intuitive zero temperature, or $\epsilon \rightarrow -\infty$, limit).

In the case of film growth, it is not clear *a priori* how to determine the substrate attraction strength $\epsilon_{\text{sub,crit}}$ for the dynamic layering transition. From the roughness behavior in Fig. 4 it can be deduced that at rather early stages of growth (i.e., at or below monolayer deposition) the transition from ISL to LBL is decided. We have investigated various observables (roughness, coverages of the first and second layer, antiphase Bragg intensity and growth number) and found that in particular for $\Theta = 1$ (i.e., after deposition of one monolayer), all these quantities show a pronounced qualitative change in behavior when plotted as functions of ϵ_{sub} (see Appendix B). Furthermore, we find a very suitable order parameter, namely the observable $\Psi_{1-2} = \Psi_1 - \Psi_2$, with Ψ_i , $i \in \{1, 2\}$ quantifying the net occupancy or filling of the first or second layer. In an LBL scenario Ψ_{1-2} will be 1, whereas in an island forming scenario its value will be close to 0. If dynamic layering is connected to the sharp equilibrium

layering transition one would expect its value to jump from 0 to 1 at $\epsilon_{\text{sub,crit}} \approx \epsilon$, and that the transition is rounded by finite-size effects. In our simulations we have found that the $\Psi_{1-2}(\epsilon_{\text{sub}})$ can be fitted quite well with a tanh curve (this is similar to the behavior of an order parameter for an equilibrium transition): We determined $\epsilon_{\text{sub,crit}}$ as the inflection point of the fitting curve (see Fig. 6: There we only show data for the CGM since the results for the SOS model are very similar).

The dependence of the critical ratio $\Upsilon_c = \epsilon_{\text{sub,crit}}/\epsilon$ on $|\epsilon|$ (shown in Fig. 7) demonstrates (i) that there is only a small difference between the CGM and the SOS model and, more importantly, (ii) that the difference to the equilibrium value $\Upsilon = 1$ increases with increasing $|\epsilon|$ at fixed Γ . This corresponds to an increasing “dynamic gap” in the onset of layering with increasing attraction strength.

The tanh fits for $\Psi_{1-2}(|\epsilon_{\text{sub}}|)$ (see Fig. 6) show that the width is increasing for increasing $|\epsilon|$ (i.e., for increasing “distance to equilibrium,” since a stronger ϵ leads to a slower exploration of the phase space). This finite width is not a finite-size effect as in equilibrium transitions, it is largely independent of the size of the lattice. This is illustrated in Fig. 8 which demonstrates that both in the SOS and the CG model for $L \geq 64$ there is no significant change in $\Psi_{1-2}(|\epsilon_{\text{sub}}|)$ when increasing L , which might be surprising considering that $L = 64$ is comparatively small. For $L \lesssim 32$ the data are very noisy and cannot be fitted very well.

The proximity of the dynamic layering transition for the CGM and the SOS models appears surprising at first glance, considering that in the CGM particles can desorb from the substrate which should be a non-negligible process at lower ϵ . From the roughness evolution in Fig. 4 we see, however, that the behavior of $\sigma(\Theta)$ is very similar for both models for substrate attraction strengths around the transition value. We rationalize this by studying in the CGM the fraction r_{nc} , the number of particles not connected to the substrate divided by the total number of deposited particles (in the SOS model, $r_{\text{nc}} = 0$ by definition). Figure 9 shows this for exemplary parameters: While during the very early stages of growth r_{nc} is substantial, it quickly drops to zero when enough material is deposited for one monolayer, i.e., when $\Theta \rightarrow 1$. Considering only disconnected particles in the first two layers (these contribute to the order parameter Ψ_{1-2}), we see that the corresponding ratio is small from the start of growth and essentially zero at $\Theta = 1$ (inset of Fig. 9). Therefore, we can expect that the occupation in the first two layers of the growing film is very similar for the CGM and the SOS models, resulting in similar roughness and order parameters.

We have analyzed the dynamic layering transition using the control parameter $\Upsilon = \epsilon_{\text{sub}}/\epsilon$, in particular to facilitate a comparison to the equilibrium wetting transition of the lattice gas model. In the dynamic model, the critical ratio most generally depends on three parameters, $\Upsilon_c = \Upsilon_c(\epsilon, \Gamma, E_{\text{ES}})$. Experimentally, the substrate attraction strength ϵ_{sub} appears to be difficult to tune for locating the transition. Within certain limits, it is easier to tune Γ by changing the deposition rate, but seeing the transition would require that the chosen substrate is not too deep in the LBL or the ISL regime. It is quite easy to control the substrate temperature T ; however, changing T influences all three variables: ϵ , $E_{\text{ES}} \propto 1/T$ and $\Gamma = D/F \propto T \exp[-E_D/(k_B T)]$ where E_D is an energetic barrier

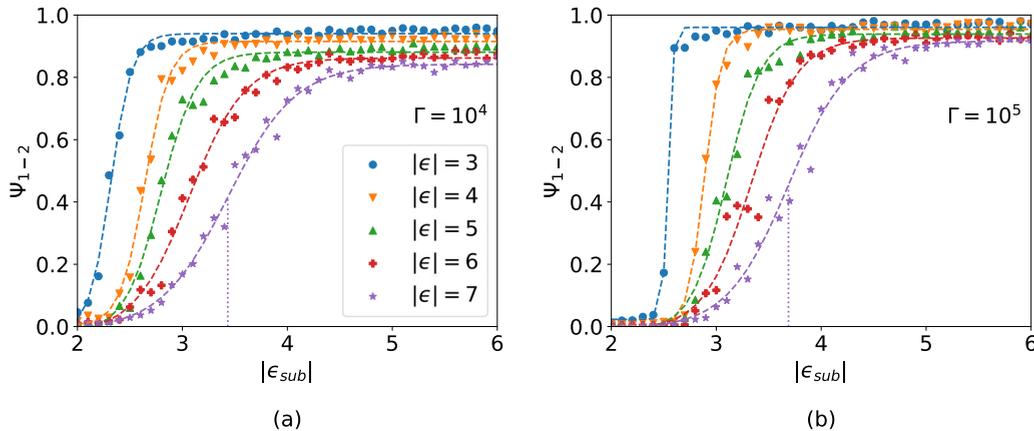


FIG. 6. Ψ_{1-2} after deposition of 1 ML in the CGM with corresponding fits for (a) $\Gamma = 10^4$ and (b) $\Gamma = 10^5$, averaged over five runs. The critical substrate attraction strength for the dynamic layering transition is determined by the x coordinate of the inflection point (dotted lines for $|\epsilon| = 7$ as an example). The legend in (a) also applies to (b). We only show data for the CGM since those of the SOS model are very similar.

for surface diffusion.¹ Therefore, temperature variations are not very suitable for locating the transition.

B. Flattening transition

In Fig. 10 we show the roughness evolution up to a total coverage $\Theta = 50$ both for the SOS model and the CGM, again for $\epsilon = -3$ and -5 , respectively, and each for a range of substrate attractions ϵ_{sub} . For weaker ϵ_{sub} (initial growth in the ISL mode), after an initial increase of the roughness (reflecting the island formation), it then decreases for intermediate times and reaches $\sigma \lesssim 1$, indicating a change to growth in LBL fashion. This behavior can be seen in both the CGM and the SOS model; however, we will see that in the SOS model it can only occur at sufficiently weak ϵ and strong ϵ_{sub} .

Reduction of the roughness occurs due to a “flattening” of the film and can be explained in simple terms by the following picture: Initial island growth at a certain deposition rate results in a finite coverage of the substrate with islands. Newly arriving particles “see” an effective substrate which is a mixture of the original one and the islands with a correspondingly increased effective ϵ_{sub} . This triggers dynamic layering, eventually leading to the substrate being completely covered in particles. For any particles arriving afterwards, growth continues as it does in a homoepitaxial system. However, this can only occur if the effects of 3D growth at short times are weak.

We call this transition ISL \rightarrow LBL. In the CGM it can be seen for all combinations of ϵ and ϵ_{sub} for which the system initially shows island formation. In the SOS model, however, we see that at these parameters [Fig. 10(b)] the roughness will (after the initial increase) decrease toward a constant value larger than 1. We call this transition ISL \rightarrow CONST. The appearance of this transition is a consequence of the restrictions in the layer-changing move in the SOS model which can only proceed one layer up or down. At weak ϵ_{sub} , the particles will initially form islands on the substrate. At later

times these will start to merge, but do so only incompletely. Trenches of depth > 1 remain between them, which can only be filled with deposition moves. This is different in the CGM where height differences (such as in the trenches) can be compensated more easily due to particles desorbing into the gas phase and statistically readsorbing at the film at positions with higher binding number. For weak ϵ_{sub} this has the dual effect of initially forming larger and fewer islands compared to the SOS model (with ensuing higher roughness) and later on smoothing the film of merged islands, resulting in LBL growth.

To quantify the times at which these transitions will occur, we found the behavior of the minimum film height or of the kurtosis of the height distribution (fourth normalized moment), depending on ϵ_{sub} , to be effective. For quantitative analysis, we use the minimum height, since this yields clearer results than the kurtosis (see Appendix C). In Fig. 11 we show examples for the evolution of the minimum film height overlaid with that of the roughness. In the CGM, the minimum film height jumps at the point where the roughness drops to values < 1 (indicating LBL behavior) and then increases linearly. In the SOS model, the minimum film height changes from being flat zero to a linear increase near the corresponding roughness

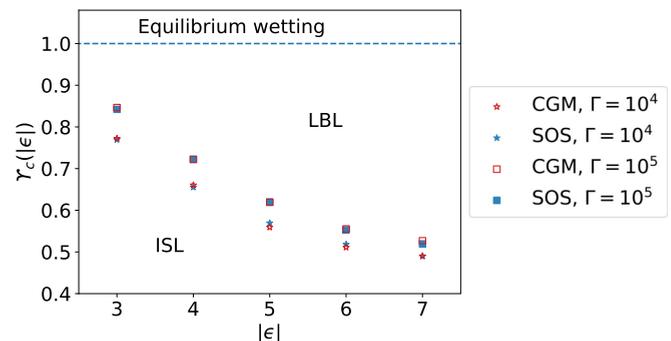


FIG. 7. The critical ratio $\Upsilon_c(|\epsilon|)$ for the dynamic layering transition at $\Gamma = 10^4$ and 10^5 in both the CGM and the SOS model. The dashed line is the approximate value 1 for the equilibrium layering transition.

¹For colloidal diffusion, one typically assumes $D \propto T \exp[-E_D/(k_B T)]$. In contrast, for metal-on-metal diffusion, one assumes $D \propto \exp[-E_D/(k_B T)]$.

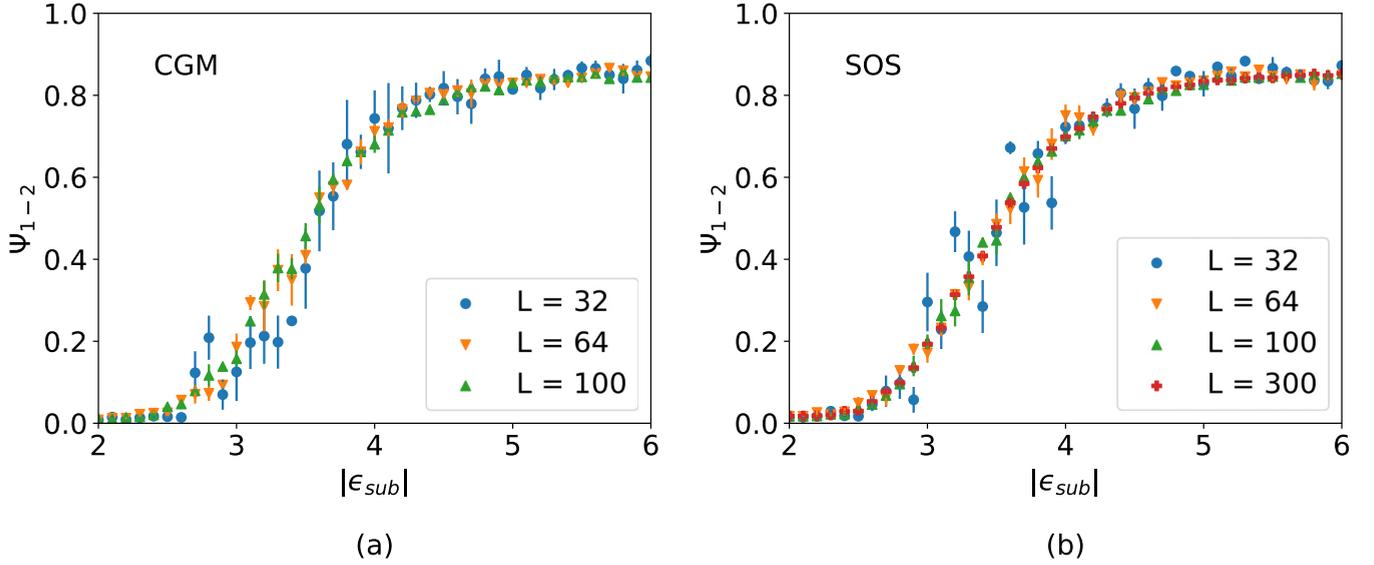


FIG. 8. The behavior of $\Psi_{1-2}(|\epsilon_{\text{sub}}|)$ at $\Gamma = 10^4$ and $\epsilon = -7$ for different system sizes. (a) CGM and (b) SOS. Data are averaged over five runs.

drop. In order to obtain numerical values for the transition time (coverage Θ_{trans}), we used different methods for the two models. For the SOS model, we average $\min. \{h(\Theta)\}$ of several runs, fit a line to the region where it increases and extract the intersection of this line with the x axis. For the CGM results, we define a fit function of the form

$$f(\Theta) = \begin{cases} 0, & \text{if } \Theta < \Theta_{\text{trans}}, \\ a\Theta + b, & \text{else} \end{cases}, \quad (4)$$

where Θ_{trans} is the transition point ISL \rightarrow LBL. Here a , b , and Θ_{trans} are free parameters which we fitted for each run. The final result for the transition time is the average over the different runs. Examples for these fits are shown in Fig. 12.

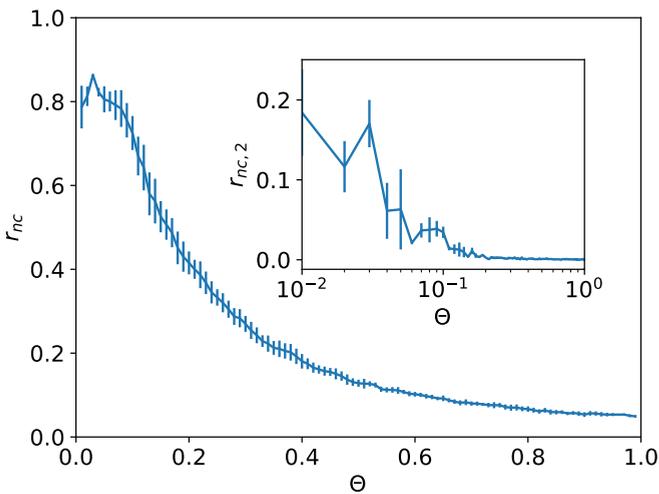


FIG. 9. The fraction r_{nc} of particles not connected to the substrate vs. Θ (total amount of deposited MLs) at $\Gamma = 10^5$, $\epsilon = -3$, $\epsilon_{\text{sub}} = -2$. The inset shows the corresponding fraction, if only disconnected particles in the first two layers are considered. We see that at $\Theta = 1$ all particles within the first two layers are in some way connected to the substrate.

The variation of the transition time Θ_{trans} with ϵ_{sub} reveals interesting behavior. As can be seen in Fig. 13, Θ_{trans} in the SOS model changes rather abruptly from a value around 10 to a value below 2. $\Theta_{\text{trans}} \sim 10$ is connected to the occurrence of the ISL \rightarrow CONST transition, whereas $\Theta_{\text{trans}} < 2$ is connected to the ISL \rightarrow LBL transition. The abrupt change thus means that there is a “transition (on substrate change) between transition scenarios (in temporal roughness evolution).” For $\epsilon = -3$, the change in Θ_{trans} occurs at a $|\epsilon_{\text{sub}}| < |\epsilon_{\text{sub,crit}}|$, i.e., at a substrate attraction strength weaker than the critical attraction strength for the dynamic layering transition. Consequently one observes the sequence in growth modes ISL \rightarrow CONST to ISL \rightarrow LBL to LBL on increasing $|\epsilon_{\text{sub}}|$ [see Fig. 10(b), going from the top curve to the bottom curve]. For $\epsilon = -5$, the change in Θ_{trans} occurs at a $|\epsilon_{\text{sub}}| \sim |\epsilon_{\text{sub,crit}}|$. This leads to a disappearance of the ISL \rightarrow LBL transition (which is “swallowed” by LBL growth from the start), i.e., one observes only the sequence ISL \rightarrow CONST to LBL on increasing $|\epsilon_{\text{sub}}|$ [see Fig. 10(d)]. In the CGM, there is only one transition scenario (ISL \rightarrow LBL), and the variation of Θ_{trans} with ϵ_{sub} is smoother (although a drop with increasing substrate attraction strength is seen as well).

C. Asymptotic growth behavior

We have analyzed quantitatively the dynamic layering transition and the flattening transition for vanishing Ehrlich-Schwöbel barrier. If Γ is not too small, then film growth in the CGM will always return to LBL growth at intermediate times, and in the SOS model there will be a finite intermediate time when the first layer is fully covered. This means that we return to homoeptaxial growth where substrate and film material are the same. In this case, we expect that the film will always roughen for very long deposition times, although for $E_{\text{ES}} = 0$ the effect is quite weak. This has been recently studied for the SOS model [10], and the following approximate scaling relation has been found:

$$\sigma \propto \Theta^\beta / (\Gamma^{3/2} [\exp(-|\epsilon|) + a]), \quad (5)$$

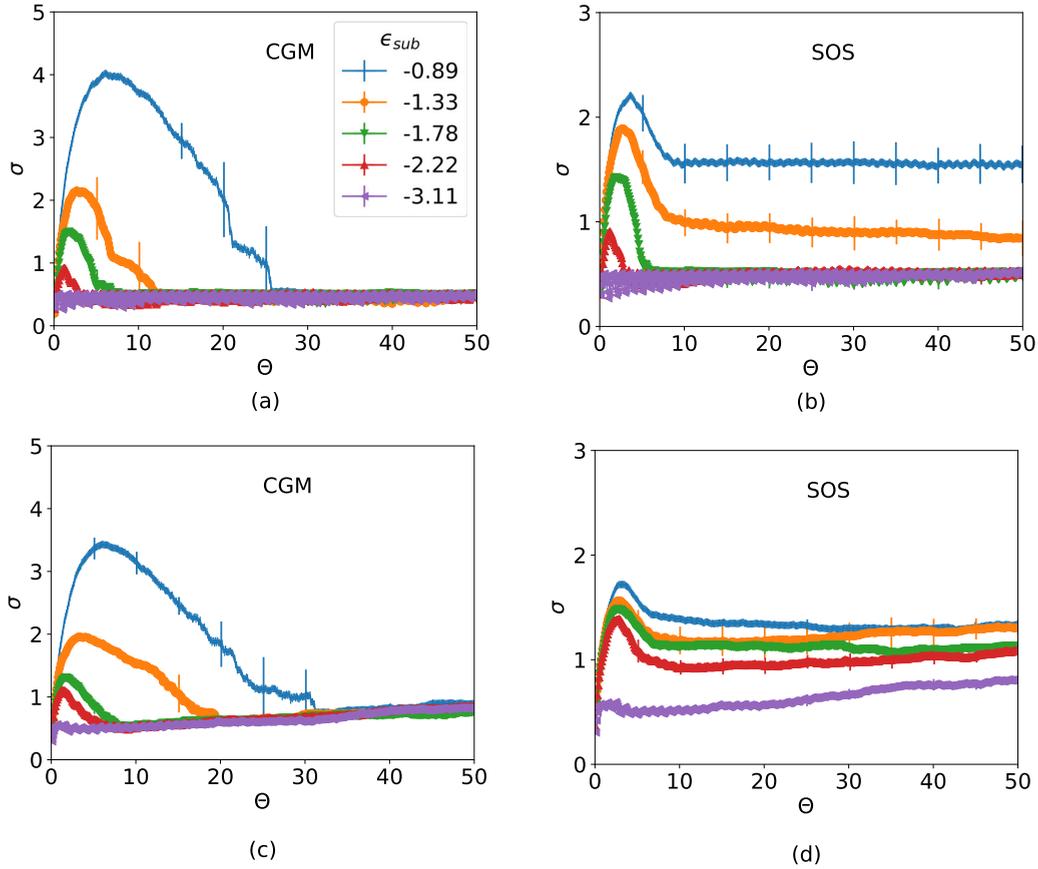


FIG. 10. Roughness evolution for deposition up to 50 ML for $\Gamma = 10^4$ and different substrate strengths ϵ_{sub} . (a) $\epsilon = -3$, CGM; (b) $\epsilon = -3$, SOS; (c) $\epsilon = -5$, CGM; (d) $\epsilon = -5$, SOS. The legend in (a) also applies to (b)–(d). Note that the maximum roughness on the y-axis differs between the CGM and the SOS model. The CGM data are averaged over 3 independent runs, the SOS data over 5.

with $\beta \approx 0.2$ and $a = 0.025$. For $|\epsilon| < -\ln a \approx 3.7$ this implies equivalent roughness evolution if

$$|\epsilon| - \frac{3}{2} \log \Gamma = \text{const}, \quad (6)$$

which should be compared to Eq. (3) for the scaling of the island density in the submonolayer regime where the factor $3/2$ is absent.

The limit $\Gamma \rightarrow 0$ in the SOS model corresponds to stochastic growth ($\beta = 1/2$). Thus, for small Γ , there is roughening or 3D growth from the start which on increasing Γ crosses over to the scenario described above.

A nonvanishing Ehrlich-Schwöbel barrier modifies these scenarios quantitatively but not qualitatively. For a given $E_{\text{ES}} > 0$ and for very small Γ (fast deposition), we start with stochastic growth. The gradual crossover to either ISL or LBL growth on increasing Γ is shifted to larger Γ compared to the case $E_{\text{ES}} = 0$. In the homoepitaxial case with $\epsilon = \epsilon_{\text{sub}}$, the gradual crossover to LBL growth has been studied in the analytic rate equation model by Trofimov *et al.* [47] and shows the continuous shift to higher Γ . This corresponds very well to the SOS simulation phenomenology. It is also clear that the ISL \rightarrow LBL transition at intermediate times still exists. It possibly occurs at larger Γ , since the necessary interlayer transport for this transition is slowed down by a nonzero Ehrlich-Schwöbel barrier, which can be compensated by larger a diffusion constant. In general, for $E_{\text{ES}} > 0$ the CGM and SOS model should also show the same qualitative phenomenology but there is

an interesting difference for large ES barriers ($E_{\text{ES}} \rightarrow \infty$). In the CGM, there is always a net interlayer transport even if $E_{\text{ES}} = \infty$ due to desorption or readsorption processes and this leads to the phenomenon of another transition, namely between LBL growth and stochastic growth. This is discussed in Appendix D.

Putting all these findings together, we have the following global scenarios for the roughness evolution in the CGM and SOS model studied here (see Fig. 14). In all scenarios, there is 3D growth for asymptotic times. For small Γ (very high deposition rates) one finds 3D growth from the start, see Fig. 14(a). For larger Γ , one must distinguish between $|\epsilon_{\text{sub}}| > |\epsilon_{\text{sub,crit}}(\epsilon, \Gamma, E_{\text{ES}})|$ and $|\epsilon_{\text{sub}}| < |\epsilon_{\text{sub,crit}}(\epsilon, \Gamma, E_{\text{ES}})|$. In the first case, one finds LBL \rightarrow 3D [initial LBL growth, followed by 3D growth, see Fig. 14(b)]. In the second case, island formation occurs from the start. For intermediate Γ , the transition from ISL back to LBL growth does not happen and the growth sequence is ISL \rightarrow 3D [see Fig. 14(c)]. For high Γ , this transition does happen and the growth sequence is ISL \rightarrow LBL/CONST \rightarrow 3D [see Fig. 14(d)]. In Sec. III B we have discussed (for $E_{\text{ES}} = 0$) under which condition the intermediate LBL or CONST regime occurs.

The schematic roughness evolution of Fig. 14 is illustrated by simulation examples using the SOS model, see Fig. 15. Here we have chosen $E_{\text{ES}} = 0$, but, as discussed before, the same scenarios can also be found for a finite ES barrier.

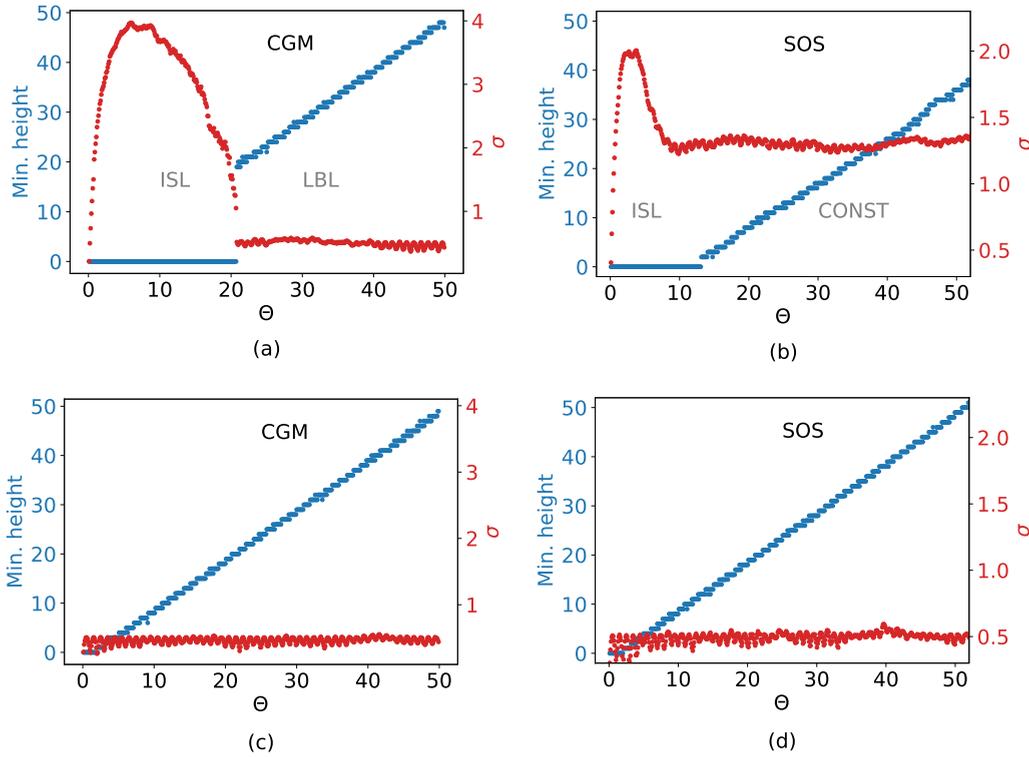


FIG. 11. Minimum film height and roughness vs. Θ in the CGM and the SOS model for [(a) and (b)] $\epsilon_{\text{sub}} = -0.89$ and [(c) and (d)] $\epsilon_{\text{sub}} = -2.67$. For $\epsilon_{\text{sub}} = -0.89$ we see that in the CGM the min. height will be 0 and then show a large jump around $\Theta = 20$, while in the SOS model there is no jump, and the min. height increases continuously after a certain point. For $\epsilon_{\text{sub}} = -2.67$ we can see such a continuous increase in both models from an early time on.

IV. COMPARISON TO EXPERIMENTAL RESULTS

In order to put the theory in a broader perspective, we shall discuss experimental results from different areas, namely “molecular thin films” and “atomic thin films.”

Growth of thin films in both categories differ strongly, since, in comparison, molecules are generally anisotropic with comparably weak interaction strengths (dominantly of vander-Waals type), whereas atoms are isotropic and typically exhibit stronger, covalent or ionic, interaction. For the comparison with experimental systems, an obvious choice would

also be heteroepitaxial growth of metallic thin films. There are indeed many studies (see, e.g., Refs. [53,54] for an overview and general considerations), but of course in these the evolution of elastic strain usually plays an important role.

Since the lattice parameter is an intrinsic property of the materials involved, which will generally differ, the role of strain cannot easily be “switched off” in the experiment. This applies in a similar and indeed more serious manner to classical semiconductor systems, for which lattice strain and the elastic response is typically much stronger than for molecular systems (see below). Our theoretical considerations might be

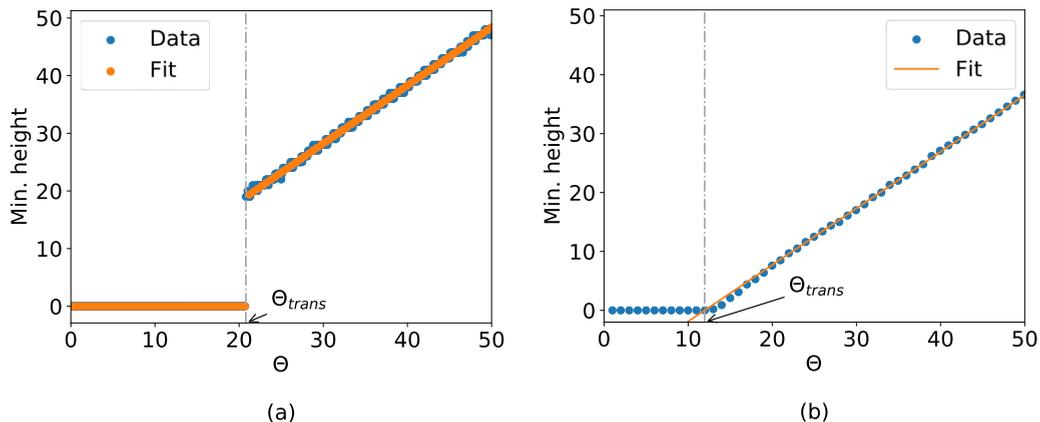


FIG. 12. Examples of fitted Θ_{trans} for $\epsilon = -3$, $\epsilon_{\text{sub}} = -0.89$, $\Gamma = 10^4$ in (a) the CGM and (b) the SOS model. The plots show the data and the fit used to determine the respective Θ_{trans} .

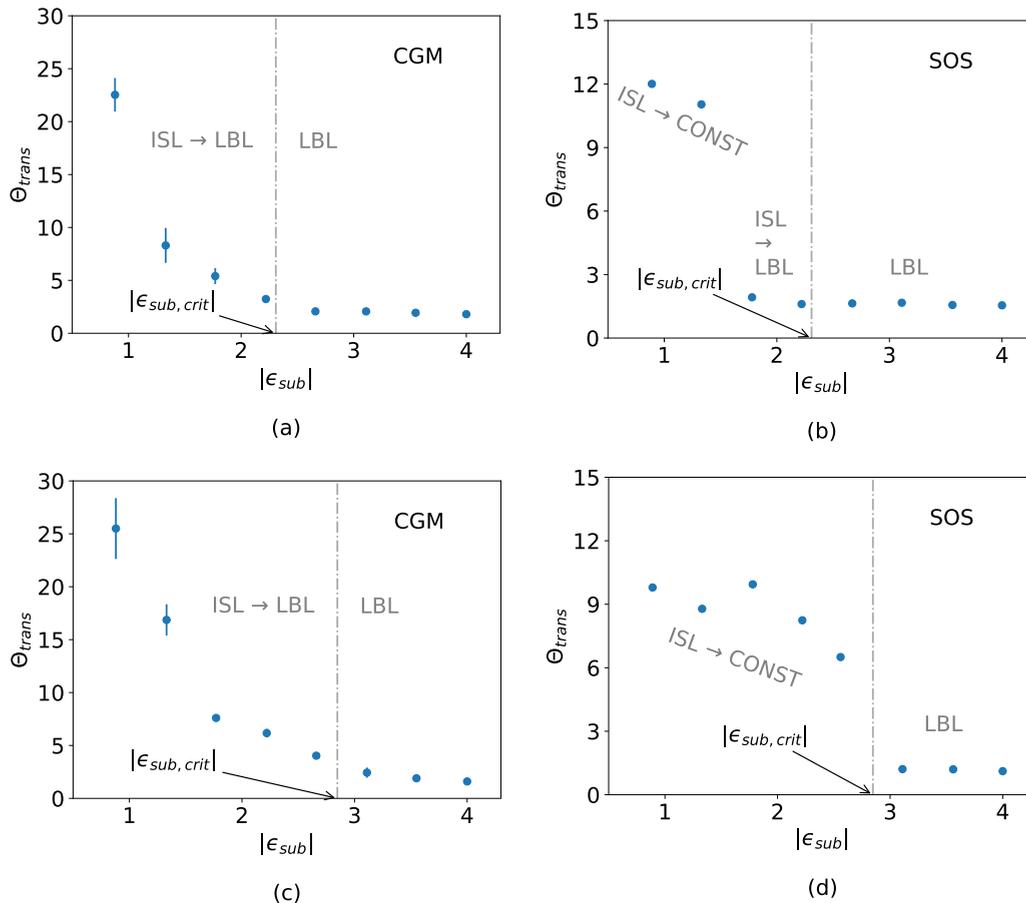


FIG. 13. Θ_{trans} plotted vs. ϵ_{sub} in the CGM and SOS model respectively for [(a) and (b)] $\epsilon = -3$ and [(c) and (d)] $\epsilon = -5$. For $\epsilon = -3$ we see that in the SOS model there is a jump in Θ_{trans} at an ϵ_{sub} which is lower than that of the dynamic wetting transition, while for $\epsilon = -5$ this jump is at a $|\epsilon_{\text{sub}}| \approx |\epsilon_{\text{sub,crit}}|$, causing the ISL \rightarrow LBL transition to disappear. In the CGM we see a smooth decrease of Θ_{trans} with an increasing ϵ_{sub} . The CGM data are averaged over 3 runs, while the SOS data are averaged over 10 runs.

employed for systems which incidentally have the same lattice parameter for substrate and film, such as, e.g., Au and Ag. Unfortunately, studies of this type are rare, and of course they would also not allow any tuning of the substrate energies.

Nevertheless, some of the general scenarios of Fig. 14 are also found in systems in which strain is part of the picture. For example, Al grown on sapphire shows a transition from 3D to 2D growth [Fig. 14(d)] after several hundred monolayers [55]. In contrast, Al grown on Si(111) at high deposition rates shows LBL growth followed by a slow roughening transition [Fig. 14(b)] [56]. These growth modes can also be found in systems with metals evaporated onto soft and disordered substrates, where strain is expected to be less important [57–59].

Molecular thin films frequently are more tolerant against mechanical strain, which makes a comparison to theory without considerations of epitaxy potentially very suitable. In fact, all of the growth scenarios depicted in Fig. 14 can be realized. Pure 3D growth or strong islanding without coalescing [Fig. 14(a)] is regularly observed for growth on 2D materials, e.g., diindenoperylene on MoS_2 [60] and pentacene or oligothiophenes on graphene [61,62]. In addition, it is found that substrates strongly interacting with the deposited molecules often exhibit a strongly bound wetting layer which saturates

the reactive surface. In the subsequent multilayer regime, again, pure 3D growth is found.

Since the first strongly bound monolayer has usually a different molecular orientation and features a completely different interaction, we have to distinguish this from classical Stranski-Krastanov growth, with a transition from LBL to 3D growth [Fig. 14(b)]. Instead, we regard the first bound monolayer here as a surface modification that induces 3D growth of the same material in the multilayer regime. Typical examples for this type of growth are pentacene on Au [63] or diindenoperylene on Au [64].

A transition from LBL growth to 3D growth is typically observed for growth on weakly interacting substrates like SiO_2 . Well-studied examples are the growth of pentacene [50,65], perfluoropentacene [66] and PTCDI- C_x [67,68] or α -sexithiophene [69] which all feature the transition from LBL to 3D within a few closed layers. The dependence of the LBL-to-3D transition on growth rate and temperature was studied for diindenoperylene [70–72] and tetracene [48]. The latter example also demonstrates that by tuning growth rate and temperature the transition of LBL to 3D can be below one monolayer changing the growth behavior effectively to pure 3D [Fig. 14(a)]. Also surface modification by self-assembled

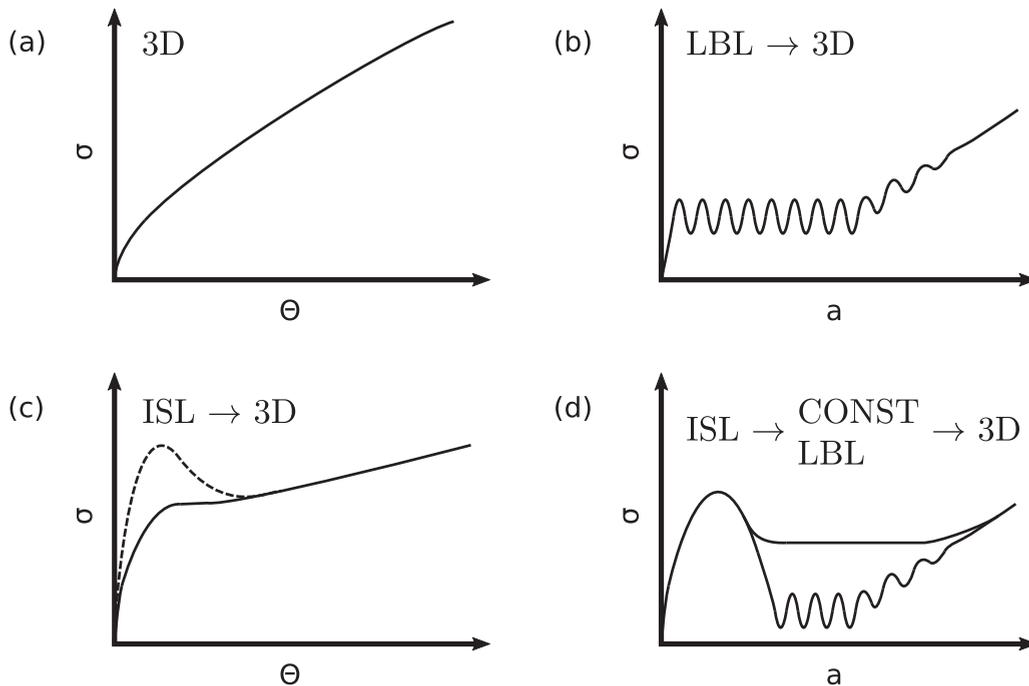


FIG. 14. Schematic representations of possible transitions. (a) Three-dimensional growth from the start for small Γ (very high deposition rates). (b) Initial LBL growth, followed by 3D growth for larger Γ and $|\epsilon_{\text{sub}}| > |\epsilon_{\text{sub,crit}}|$. (c) Initial ISL growth, followed by 3D growth for intermediate Γ and $|\epsilon_{\text{sub}}| < |\epsilon_{\text{sub,crit}}|$. (d) Initial ISL growth, intermediate LBL or CONST growth, followed by 3D growth for high Γ and $|\epsilon_{\text{sub}}| < |\epsilon_{\text{sub,crit}}|$. The intermediate growth modes can be summarily termed as 2D growth.

monolayers may modify the transition thickness from LBL to 3D [73,74].

Rod-like compounds which feature an LB-to-3D transition are mostly those growing in an upright-standing mode on weakly interacting substrates. In that case the molecule–molecule interaction in the plane (π - π overlap) is stronger than the substrate–molecule interaction resulting in LBL growth. In contrast, growth of such a material on a reactive metal surface usually results in 3D growth as explained above. Exceptions are either compounds with a strong tendency to lie flat on the substrate such as PTCDA, which features an LBL-to-3D transition on Ag [6] or the spherical compound C₆₀ which has an isotropic potential [39].

Coalescing of islands at later stages with a clearly observed subsequent LBL mode [Fig. 14(d)] is observed rarely. One example are nearly amorphous thin films of rubrene on SiO₂ where the coalescing starts after approximately 5–10 monolayers [51]. In addition, for crystalline films of picene the island coalescing was observed at approximately 20–40 layers depending on growth conditions [75–77].

For the sake of a final quantitative illustration summarizing this overview, in Fig. 16 we show experimental roughness data from the growth of molecular thin films on amorphous substrates. These correspond to three of the four growth scenarios of Fig. 14. For the ISL \rightarrow 3D growth scenario, we were unable to find experimental data covering the range of film heights needed to detect the transition from island to 3D growth. However, we think that the growth of C₆₀ on SiO₂ and the growth of picene at ambient temperatures are good candidates for this scenario. It is known that C₆₀ is a strong island former. For picene the coalescing of islands is demonstrated in Refs. [75–77]. However, no continuous data set for

all thicknesses is available. Due to limitations of the x-ray reflectometry methods quantitative results for the roughness are available at intermediate time (where it is larger than expected from Poisson growth hence supporting the island picture). It is not possible to extract the roughness of such films at very short times nor at long times where the film is very rough. At long times, AFM pictures show significant roughening but post growth effects would need to be considered. We remark in passing that quantitative roughness data are only available for a fraction of the plethora of thin-film studies.

V. SUMMARY AND CONCLUSION

In this work we have investigated thin-film growth in simple lattice gas models where the substrate is energetically different from the film, and substrate and film phase are defined on the same simple-cubic lattice (no genuine heteroepitaxy, i.e., no strain effects). The investigated models are a SOS model (with no vacancies or overhangs in the growing film) and a CGM where particles can desorb from the film, diffuse in the gas phase above the film, and reabsorb again on the film. The latter is suitable for describing colloidal film growth in solutions.

For small to intermediate deposition times (up to an equivalent of about 10–20 monolayers) and not-too-fast deposition rates, the growth modes are ISL and LBL growth. In both the CGM and the SOS model, we have identified two dynamical transitions in this regime of small to intermediate deposition times. The first (“dynamic layering transition”) describes a transition from ISL to LBL growth as a function of the reduced substrate strength $\Upsilon = \epsilon_{\text{sub}}/\epsilon$ and can be viewed as the dynamical counterpart of the equilibrium

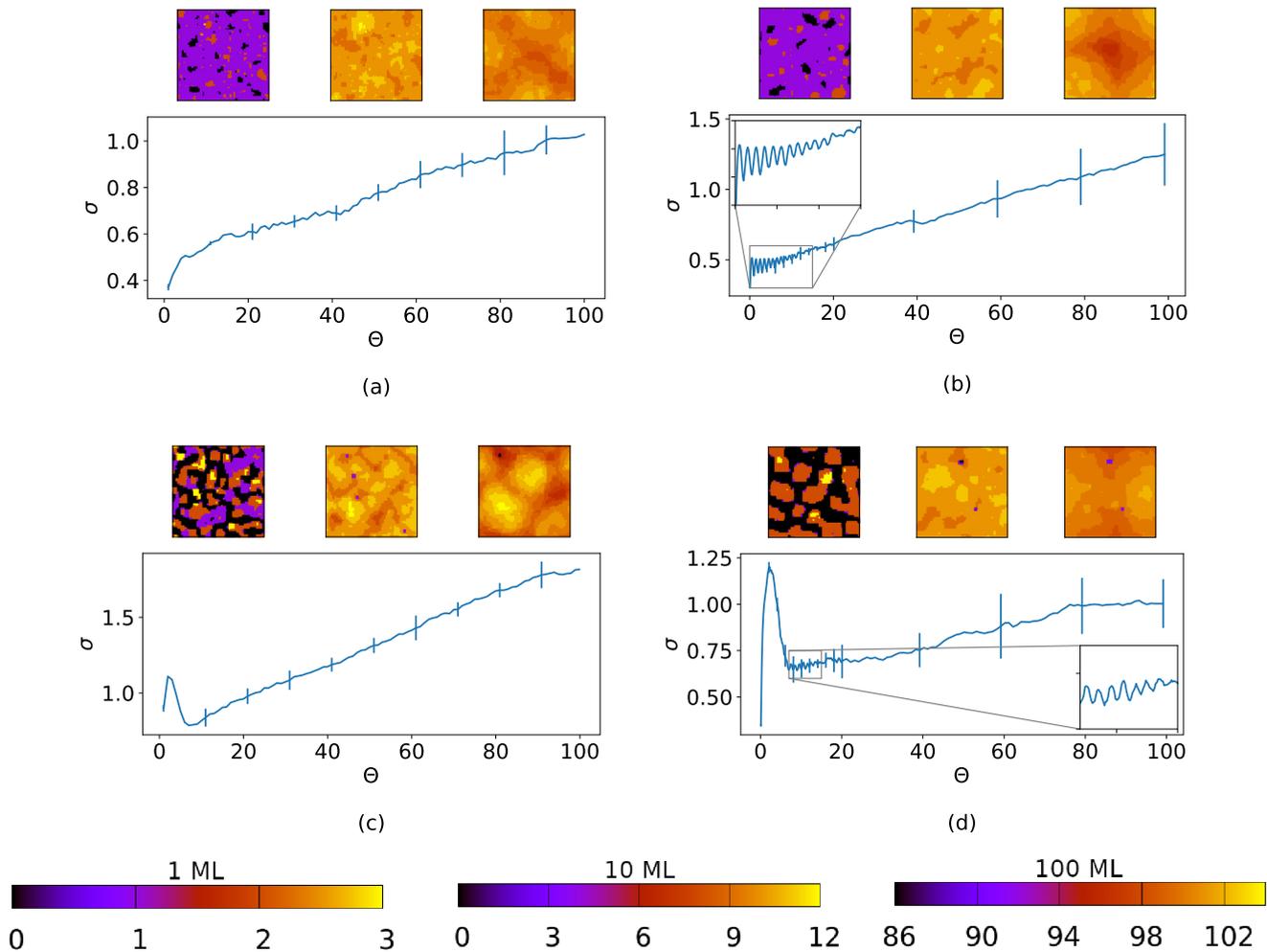


FIG. 15. Examples for the growth modes presented in Fig. 14, all for the SOS model. Vertical lines indicate statistical errors, deduced from 5 independent runs for each parameter set. (a) Three-dimensional growth at $\Gamma = 10^3$, $\epsilon = -3$, $\epsilon_{\text{sub}} = -3.56$; (b) LBL \rightarrow 3D at $\Gamma = 10^4$, $\epsilon = -5$, $\epsilon_{\text{sub}} = -3.56$; (c) ISL \rightarrow 3D at $\Gamma = 10^3$, $\epsilon = -5$, $\epsilon_{\text{sub}} = -2.22$; (d) ISL \rightarrow LBL \rightarrow 3D at $\Gamma = 10^4$, $\epsilon = -4$, $\epsilon_{\text{sub}} = -2.22$. Above each roughness plot are three height maps of representative runs at $\Theta = 1, 10, 100$

wetting transition. The latter can only depend on the particle interaction strength ϵ , and is nearly independent of it for larger $|\epsilon|$ [located at $\Upsilon(\epsilon) \approx 1$]. The dynamic transition, however, depends in general on the three parameters ϵ , Γ

(ratio of diffusion to deposition rates) and E_{ES} (Ehrlich-Schwöbel barrier for interlayer diffusion). It is found at lower values of Υ compared to the equilibrium transition, and the difference increases with increasing ϵ and decreasing Γ .

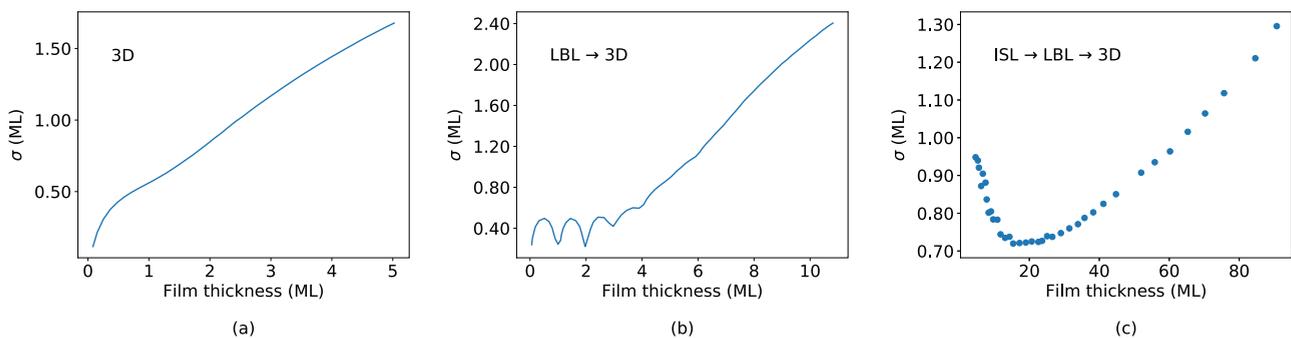


FIG. 16. Experimental *in situ* measurements of roughness vs. coverage showing different growth modes (a) tetracene on SiO_2 showing 3D growth [48] (1 ML \equiv 13.4 Å [49]), (b) pentacene on SiO_2 showing LBL \rightarrow 3D behavior [50] (1 ML \equiv 15.4 Å), (c) rubrene on SiO_2 showing ISL \rightarrow LBL \rightarrow 3D behavior [51] (1 ML \equiv 13.4 Å in an orthorhombic polymorph crystal [52]). Note, however, that in these experiments the rubrene films were amorphous)

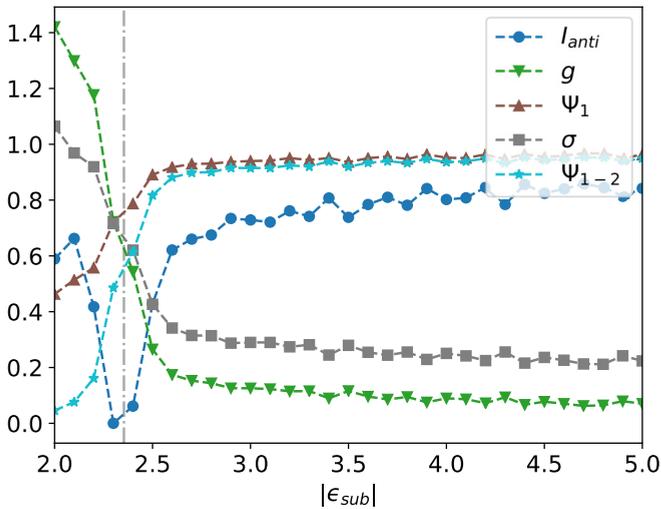


FIG. 17. Values of several eligible observables after deposition of 1 ML in the CGM. Plotted are the antiphase Bragg intensity I_{anti} , the filling of the first layer Ψ_1 , the film roughness σ , and the difference of the filling of the second and first monolayer Ψ_{1-2} . All these observables show a change in behavior roughly at the same ϵ_{sub} ; however, Ψ_{1-2} varies smoothly around this point and allows us to fit a tanh to the values and extract the inflection point.

The second transition (“flattening transition”) describes the transition from initial ISL growth back to LBL growth at an intermediate transition time. Physically, the transition is connected with the coalescence of islands and manifests itself in a drop in film roughness at the transition time. In the SOS model and depending on the specific parameters, the roughness occasionally only drops to a constant value, reflecting island coalescence with residual trenches which can be filled only by deposition.

For very long deposition times, film growth will always show roughening (3D growth) which has been already studied earlier (see, e.g., Ref. [1] for an overview). Combined with the results for small to intermediate deposition times, we have identified four global scenarios for the evolution of roughness, which are depicted in Fig. 14. These are [Fig. 14(a)] 3D growth for all times, [Fig. 14(b)] initial LBL growth followed by (weak) 3D growth, [Fig. 14(c)] initial ISL growth

followed by 3D growth, and [Fig. 14(d)] initial ISL growth with a transition to intermediate LBL growth (or growth with trenches) and followed by 3D growth. Interestingly, scenario (b) is akin to SK growth. SK growth is commonly related to genuine heteroepitaxy: The incommensurability of the substrate and film lattices leads to the build-up of mechanical stress in LBL growth, which is released after deposition of a few layers, causing the smooth film to break-up into islands (Refs. [32–34]). Our results suggest that SK growth can also occur in growth on amorphous substrates where strain would be absent.

We have discussed these results with respect to existing experimental findings. In thin-film molecular growth (with weaker interparticle interactions), the four growth scenarios can all be identified, and these also depend on the substrate interaction energy and growth kinetics. This points to a relative unimportance of molecular anisotropy with regard to the global roughness evolution. The epitaxial growth of strongly interacting compounds like metals and inorganic semiconductors depends critically on the lattice matching of substrate and thin-film- and strain-related issues, which are not incorporated in our simple approach. Nevertheless, there are several examples in the literature, which exhibit 3D to 2D or 2D to 3D growth mode transitions similar to our description.

While the dynamic transitions and the global growth scenarios are very similar for the CGM and the SOS model, differences can be found in cases where desorption and readorption are important. As an example, we discussed the case of infinite Ehrlich–Schwöbel barrier (no direct interlayer changing moves). In the SOS model, this leads to stochastic growth, while in the CGM interlayer diffusion is still possible as a multistep process via the gas phase. In the CGM this leads to the appearance of another transition for strongly attractive substrates: For low interaction strengths $|\epsilon|$ there is initial island growth which rather abruptly changes to stochastic growth on increasing $|\epsilon|$.

The “dynamic gap” between the dynamic and equilibrium layering transition also implies that monolayer films can be prepared by deposition, but would be subject to dewetting if deposition was stopped. This process has been studied, e.g., in Refs. [78,79]. Likewise, smooth multilayer films may be subject to strong postgrowth roughening. This is known for the growth of rubrene films: As discussed, these show the ISL

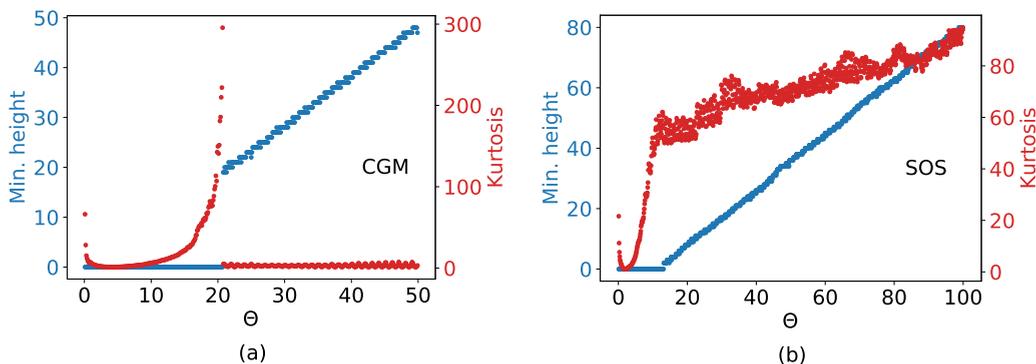


FIG. 18. Comparison of Min. height and kurtosis of the height distribution, characterizing the flattening transition, at $\Gamma = 10^4$, $\epsilon = -3$, $\epsilon_{sub} = -0.89$ in (a) the CGM and (b) the SOS model.

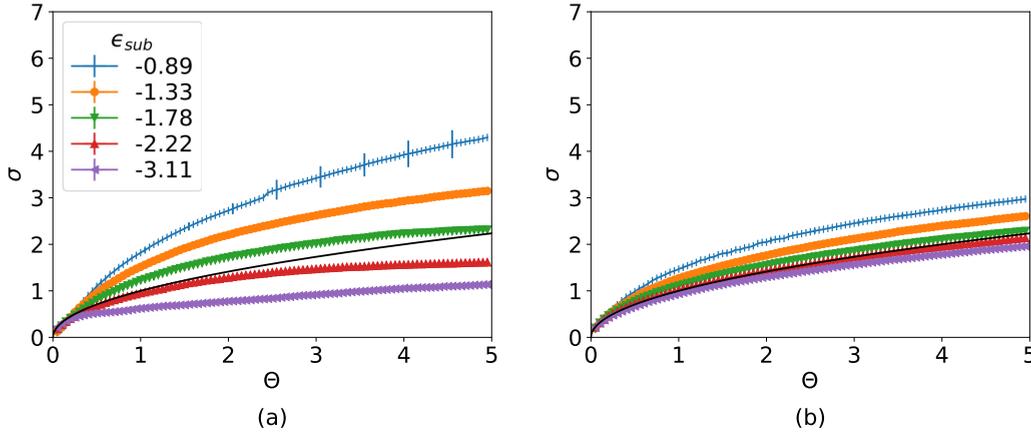


FIG. 19. Evolution of roughness in the CGM $\epsilon_{ES} = \infty$ at $\Gamma = 10^4$ and for different ϵ_{sub} . (a) $\epsilon = -3$, (b) $\epsilon = -5$. The black line denotes the statistical roughness evolution $\sigma = \sqrt{\Theta}$.

→ LBL → 3D growth mode [see Fig. 16(c)] when measured in real-time, but strong dewetting of the smooth film into a variety of patterns is observed on the timescale of a few days to a month [80]. Leaving the subject of one-component films, one can expect that the phenomenology of dynamic transitions and dewetting behavior becomes much richer when going to growth in binary systems [81,82]. With regard to growth with organic molecules, an extension of the lattice models to anisotropic interactions would also be desirable which can be accomplished by using anisotropic, energetic interaction parameters or using lattice rods to capture steric effects [83–85].

ACKNOWLEDGMENT

We gratefully acknowledge the financial support of the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG).

APPENDIX A: ISING MODEL AND LATTICE GAS

The Ising model in 3D on a semi-infinite SC lattice bounded by a planar substrate is defined by the Hamiltonian

$$\mathcal{H}_{Is} = J \sum_{\langle ij \rangle} \sigma_i \sigma_j + H \sum_i \sigma_i + H_1 \sum_{surf,i} \sigma_i, \quad (A1)$$

where $\sigma_i = \{1, -1\}$ is a spin variable, J is the nearest neighbor coupling strength ($\langle ij \rangle$ label nearest neighbor sites), H is a bulk (magnetic) field and H_1 is a surface field (the sum over spins in the corresponding term only extends over spins adjacent to the substrate).

On the other hand, the Hamiltonian of the lattice gas (as used here, with a bulk external field $V^{ext}/(k_B T) \equiv -\mu$) is defined by

$$\frac{\mathcal{H}_{lg}}{k_B T} = \epsilon \sum_{\langle ij \rangle} n_i n_j - \mu \sum_i \sigma_i + \epsilon_{sub} \sum_{surf,i} \sigma_i, \quad (A2)$$

where $n_i = \{1, 0\}$ is a lattice site occupation variable. On defining $\sigma_i = 2n_i - 1$, both Hamiltonians are equivalent (up to an unimportant constant) if the following identifications are

made:

$$\epsilon = \frac{4J}{k_B T}, \quad \epsilon_{sub} = \frac{2J + 2H_1}{k_B T}, \quad \mu = \frac{-2H + 12J}{k_B T}. \quad (A3)$$

Using these identifications, the wetting diagram of Ref. [46] [Fig. 1(C)] corresponds to Fig. 5 in the present work.

APPENDIX B: COMPARISON OF POSSIBLE ORDER PARAMETERS FOR LOCATING THE DYNAMIC LAYERING TRANSITION

In order to quantify the critical ϵ_{sub} for the dynamic layering transition, we compared the values of several possible observables after deposition of 1 ML. These observables included among others the roughness σ , the layer filling Ψ_i of the first and second layer, the growth number [21]

$$g = \frac{\sum_{n=1}^{\infty} |\Theta_n - \Theta_{n,LBL}|}{\sum_{n=1}^{\infty} |\Theta_{n,stat} - \Theta_{n,LBL}|} \quad (B1)$$

(where Θ_n is the measured coverage in layer n , $\Theta_{n,LBL}$ is the coverage at this height assuming perfect LBL growth, and $\Theta_{n,stat}$ is the coverage at this height assuming completely statistical growth), and the antiphase Bragg intensity, which is defined [21] as

$$I_{anti}(\Theta) = \left| \sum_{i=0}^{\infty} (-1)^i [\Psi_i(\Theta) - \Psi_{i+1}(\Theta)] \right|^2 \quad (B2)$$

(where $i = 0$ denotes the substrate layer, i.e., Ψ_0 is always 1). The growth number g is a measure of whether a film grows in an LBL fashion ($g = 0$), in a Poisson manner ($g = 1$) or in an intermediate manner. The antiphase Bragg intensity is the intensity of, e.g., reflected x rays at the anti-Bragg point, where reflections from neighboring layers interfere destructively. This leads, e.g., to $I_{anti}(\Theta)$ showing oscillations when observing films growing in an LBL fashion [86].

All of these show a change in behavior around the same ϵ_{sub} ; however, in Fig. 17 we can see that the behavior of Ψ_{1-2} is most intuitive for signaling a transition: We may comfortably fit a tanh to the data points. Hence we chose to use this observable to quantify the dynamic transition point.

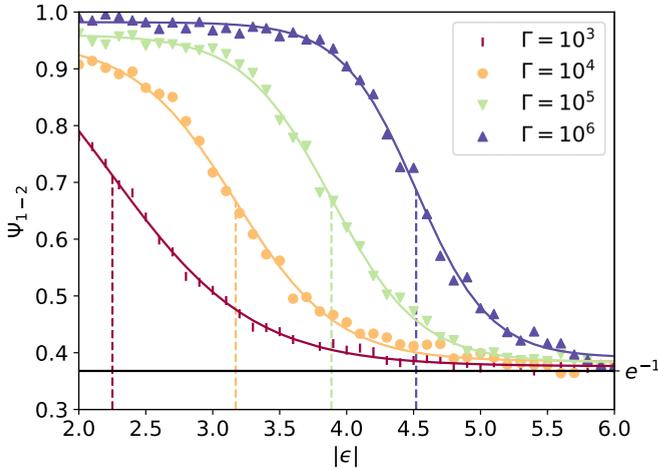


FIG. 20. $\Psi_{1-2}(|\epsilon|)$ after deposition of 1 ML in the CGM at $\epsilon_{\text{sub}} = -10^6$. The dashed lines indicate the inflection points at the respective Γ .

APPENDIX C: COMPARISON OF MULTILAYER ORDER PARAMETERS

To quantify where the ISL \rightarrow LBL and the ISL \rightarrow const transition occur, we considered the minimum height of the film and the kurtosis which is the normalized fourth moment of the height distribution.

In Fig. 18 we can see that both observables show a change in behavior at the same coverage Θ . However, only the minimum height allows us to clearly pinpoint the exact transition time (the earliest time at which $\min h > 0$), while the change in behavior of the kurtosis is, e.g., not easily quantifiable in the SOS model.

APPENDIX D: INFINITE EHRLICH-SCHWÖBEL BARRIER

As discussed in Sec. III C the generic growth modes for both the CGM and the SOS model at not too small Γ are as follows: At short times, both systems will show either island growth or LBL growth, while at long times, they will both show 3D growth. We can, however, already see a deviation at short times in the special case of an infinite ES barrier. In the

SOS model, this means that interlayer diffusion is prohibited, which leads to the well known roughening behavior of $\sigma \propto \Theta^{1/2}$.

On the other hand, interlayer diffusion is still possible in the CGM, albeit as a multistep process in which particles will first detach from the film, perform diffusion moves inside the gas phase, and later reattach to the film, possibly in a different layer. This means that the ES barrier in this system is effectively lowered to a finite value, leading to a strong deviation from the behavior in the SOS model. In Fig. 19 this is illustrated for two interparticle attraction strengths $\epsilon = -3$ and -5 and for a range of substrate attractions ϵ_{sub} . For small $|\epsilon_{\text{sub}}|$, the roughness grows faster than in stochastic growth, reflecting island formation. For larger $|\epsilon_{\text{sub}}|$ the roughness decreases. For lower ϵ it can go significantly below the roughness from stochastic growth, reaching $\sigma \lesssim 1$ as in LBL growth. For larger ϵ it saturates near the $\sigma \propto \Theta^{1/2}$ curve from stochastic growth. Other observables, such as the filling of each layer vs. time also confirm the saturation in the stochastic growth mode.

To study the transition from LBL-like behavior to stochastic growth for very attractive substrates, we compute $\Psi_{1-2}(|\epsilon|)$ after deposition of 1 ML (as in Sec. III A) and again find a tanh-like behavior of the observable, as shown in Fig. 20. Here we set $\epsilon_{\text{sub}} = -10^6$, i.e., quasi-infinite, so particles which reach the substrate will stay within the first layer.

At low $|\epsilon|$, Ψ_{1-2} is close to 1, i.e., almost all particles are confined to the first monolayer. This is expected, since particles in the second layer may step down at these parameters via a multistep process. On increasing $|\epsilon|$, Ψ_{1-2} goes to $\exp(-1)$ which is the value corresponding to stochastic growth when no interlayer diffusion is possible. This indicates that here the interparticle attraction is too strong for a significant amount of particles to desorb from the film.

The shape of $\Psi_{1-2}(|\epsilon|)$ again allows to fit a tanh curve and identify the inflection point as the critical ϵ above which the system will grow via stochastic growth. This critical attraction strength increases with increasing Γ and should disappear for $\Gamma \rightarrow \infty$. In this limit (growth rate going to zero) the particles will always be able to desorb into the gas and then attach to the substrate in the first layer where they will be effectively trapped, i.e., the stochastic growth mode will never occur.

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