Particle-resolved dynamics during multilayer growth of C\textsubscript{60}

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Using large-scale kinetic Monte-Carlo (KMC) simulations, we investigate the non-equilibrium surface growth of the fullerene C\textsubscript{60}. Recently, we have presented a self-consistent set of energy barriers that describes the nucleation and multilayer growth of C\textsubscript{60} for different temperatures and adsorption rates in quantitative agreement with experiments [Bommel et al., Nat. Comm. (2014), in press]. We found that C\textsubscript{60} displays lateral diffusion resembling colloidal systems, however it has to overcome an atom-like energetic step-edge barrier for interlayer diffusion. Here, we focus on the particle-resolved dynamics, and the interplay between surface morphology and particle dynamics during growth. Comparing C\textsubscript{60} growth with an atom-like system, we find significant differences in the evolution of the surface morphology, as well as the single-particle dynamics on the growing material landscape. By correlating the mean-squared-displacement of particles with their current neighbourhood, we can identify the influence of the different time scales that compete during growth and can pinpoint the differences between the two systems.

I. INTRODUCTION

Grown structures of nanometre-scale organic molecules are the cornerstone of organic semiconductor device constructions. The desired morphologies of organic molecules in such applications range from ultra-thin crystalline films,\textsuperscript{1} to islands, nanowires,\textsuperscript{2} and crystallites.\textsuperscript{3} Indeed, it is now well established that the morphology, combined with the type and structure of the substrate,\textsuperscript{4} determines the device functionality in terms of electron transport, charge carrier mobilities,\textsuperscript{5} and band gap energies.\textsuperscript{6} These features are, in turn, strongly influenced by morphological imperfections, which easily arise during the (non-equilibrium) growth process of organic structures on the substrate. It is therefore crucial to understand on a microscopic (molecular) level the entire process of formation of such organic-molecule structures from growth towards the final equilibrium state.

From the experimental side, information on the morphology of the organic component is obtained e.g., via atomic force,\textsuperscript{7,8} and scanning electron microscopy,\textsuperscript{9} Raman scattering,\textsuperscript{10} X-ray scattering,\textsuperscript{11}\textsuperscript{12} and electron microscopy.\textsuperscript{13,14} In particular, real-time X-ray scattering can be used to monitor the film formation in situ and thus gives important information about the system’s behavior on its way towards thermal equilibrium. From theoretical side, the techniques employed to investigate equilibrium (or even groundstate) structures of organic molecules range from ab-initio density functional theory (DFT)\textsuperscript{13} over atomistically resolved Molecular Dynamics (MD) simulations\textsuperscript{13} to coarse-grained Monte Carlo (MC) simulations\textsuperscript{10} (see\textsuperscript{12} for a recent review). Growth processes are typically studied via kinetic Monte Carlo (KMC) simulations\textsuperscript{15} and rate equations (see, e.g.,\textsuperscript{16}).

The above examples illustrate that the structure formation of organic molecules is a very active field of research. However, contrary to situation for atomic systems\textsuperscript{20} a comprehensive understanding of corresponding organic-molecule systems is still missing. From the theoretical perspective, one major challenge is the molecule’s anisotropy which strongly increases the configurational space in equilibrium sampling, as well as the space of possible movements during surface growth. Another challenge, particularly for MD and MC simulations relying on classical force fields, arises due to the typically complicated charge distributions and polarizability effects characterizing many organic molecules.

In the present paper we investigate, based on particle-resolved KMC simulations, the growth of molecular films composed of C\textsubscript{60} (fullerene). In particular, we aim at exploring the single-particle dynamics including free motion, caging, and detaching from neighbours, accompanying multilayer growth. First steps towards unravelling C\textsubscript{60} multilayer growth have been taken in Ref.\textsuperscript{10} where we developed, together with experiments, a KMC model capable of describing various real-space data.

Application-wise, C\textsubscript{60} is a key component to semiconductor devices such as transistor and solar cells,\textsuperscript{21} because of its high electron yield and photophysical properties.\textsuperscript{22,23} From a more conceptual perspective, C\textsubscript{60} is clearly one of the easiest representatives within the material class of organic molecules due to its nearly spherical shape. Indeed, at the temperatures considered in our study C\textsubscript{60} is known to rotate freely not only in the fluid phase, but also in the bulk crystal\textsuperscript{24} and in one-dimensional confinement.\textsuperscript{25} Thus, one may expect nearly-free rotations also in film-like geometries. Moreover, since a C\textsubscript{60} molecule involve only carbon atoms, partial charge effects are not important. All these features suggest to view C\textsubscript{60} rather as a particularly large atom (with a diameter of about one nanometre) than as a large organic molecule.

However, besides size and internal structure there is another important difference between C\textsubscript{60} molecules and atoms: the range of the effective, i.e. angle-averaged, attractive interaction between two C\textsubscript{60} molecules is much smaller than the usual van-der Waals interaction (decaying as $r^{-6}$, $r$ being the separation) between atoms.\textsuperscript{26,27} This short range of attraction has important consequences for the overall equilibrium phase behavior; in
particular, C\textsubscript{60} lacks a liquid phase\textsuperscript{33} but tends to form a gel phase\textsuperscript{31}. In that sense, C\textsubscript{60} rather behaves like a system of colloids, where short-range attraction (stemming from depletion effects) is in fact quite common.

Here we are interested in C\textsubscript{60} growth. Earlier theoretical studies in this area have focused on aspects such as determination of step-edge barriers and potential landscapes (yielding diffusion rates) from DFT, see, e.g.\textsuperscript{32,33}. Studies addressing the surface morphology have often been restricted to a coverage of less than one monolayer\textsuperscript{34,35}. Note that this contrasts the situation for atomic systems where growth phenomena for both, monolayers and multilayers have been studied intensely for a wide range of systems\textsuperscript{36–38}. These studies include even subtle phenomena such as concerted gliding of island\textsuperscript{39} or direction-resolved step-edge diffusion\textsuperscript{40,41}.

In our recent study we have obtained, together with real-time experiments\textsuperscript{42,43}, a consistent set of energy-barrier parameters for KMC simulations which describe measurable morphological quantities such as island density and layer coverage as functions of time. Interestingly, these energy parameters reflect again the intermediate role of C\textsubscript{60} between atoms and colloids: While the step-edge diffusion barrier is close to what one expects for atoms, the binding energy stemming from attractive interactions is much smaller, reflecting indirectly the much longer range of attraction. In the present study we focus on the interplay between morphology and the single-particle dynamics during growth. Another main objective is to identify differences between dynamical properties of C\textsubscript{60} with that of comparable atomic systems.

The remainder of the paper is organized as follows. In Sec. II we introduce the simulation techniques and target quantities considered in this study. We also propose a way to compare C\textsubscript{60} and atom-like systems in terms of energy-barrier arguments. Section III A gives an overview of KMC results for the surface morphology, followed by a detailed discussion of global (Sec. III B) and single-particle (Sec. III C) dynamical quantities. The paper closes with a summary in Sec. IV.

II. METHOD

A. Simulation method

We employ event-driven kinetic Monte Carlo simulations, using the N-fold algorithm\textsuperscript{44} (see Ref.\textsuperscript{10} for a review). This allows us to access large surfaces (with O(10\textsuperscript{6}) lattice sites) with molecular resolution. The free diffusion time, that is the average time span a particle takes for one diffusion step if it is not interacting with lateral neighbours, is O(1\mu s) (see e.g.\textsuperscript{11}). In total, however, the simulations cover the experimentally relevant range of minutes to hours.

During the growth process particles adsorb on the surface with a constant effective adsorption rate $f = f_{\text{adsorb}} - f_{\text{desorb}}$ and diffuse on the surface, until they become immobile due to interaction effects. Finally they are buried under the next grown layer. The diffusion process of a particle from site $i$ to site $j$ is given through the rate determined in the Clarke-Vvedensky bond-counting Ansatz\textsuperscript{43,44}.

$$r_{i,j} = \frac{2k_B T}{h} \exp \left( -\frac{E_{\text{free}} + n_i E_n + s_{i,j} E_{\text{ES}}}{k_B T} \right),$$  

(1)

where $k_B$ is the Boltzmann constant, $T$ is the temperature and $h$ is the Planck constant. We choose the prefactor $\nu_0 = 2k_B T/h$ in accordance with previous studies\textsuperscript{45,47}. As seen from Eq. (1), the diffusion rate $r_{i,j}$ depends exponentially on the total energy barrier the particle has to overcome to reach site $j$. This energy barrier consists of a contribution for free diffusion, $E_{\text{free}}$, a contribution arising from the interaction with the $n_i$ nearest neighbour particles, $E_n$, and an Ehrlich-Schwoebel energy barrier, $E_{\text{ES}}$. The latter is relevant for trajectories that lead across step edges, i.e., $s_{i,j} = 1$ when crossing step edges, otherwise $s_{i,j} = 0$. We note that the restriction of the interaction term to the nearest neighbours alone is consistent with the fact that the distance-dependent attraction between C\textsubscript{60} molecules is relatively short-ranged compared to the molecular diameter\textsuperscript{33}.

The simulated time progresses by a time step $\tau$ after each event. This time step is of stochastic nature, and it is weighted with the rate of change of the whole system $r_{\text{system}}$. The latter is defined as the sum of all possible process rates $r_{i,j}$ plus the adsorption rate $f$. Specifically, we have

$$\tau = \frac{-\ln(R)}{r_{\text{system}}},$$  

(2)

where $R \in [0,1]$ is a random number, and

$$r_{\text{system}} = \sum_{i=1}^{N} \left( \sum_{j=1}^{6} r_{i,j} + f \right).$$  

(3)

In Eq. (3), $N$ is the number of surface sites in the system. In accordance to experiments\textsuperscript{10}, we simulate the growth process on a triangular lattice which is equivalent to the fcc(111) lattice face of a bulk C\textsubscript{60} crystal. Interstitial sites are not considered. Furthermore, we assume that the growth process is free of defects in the sense that particles can only sit on lattice sites and cannot form overhangs. If particles reach sites, which are not supported by three “base particles” in the underlying layer, they relax to surrounding lattice sites with probabilities proportional to the corresponding diffusion rates $r_{i,j}$.

We also note that our simulation does not take into account coordinated, simultaneous motion of particle clusters. Previous studies\textsuperscript{39} have indicated that consorted cluster diffusion influences the growth only during the very initial phase of island nucleation, when the particle clusters are small. Furthermore, in a self-learning KMC study of the system Cu/Cu(111), Karim et al.\textsuperscript{48} found that the diffusion barriers of clusters scales nearly
relatively small adsorption rate \((f = 0.1 \text{ ML min}^{-1})\) as a function of the average surface height \(\bar{h} = f \times t\).

![Graph](image)

FIG. 1. (color online) Island density for \(T = 40^\circ\text{C}\) and a relatively small adsorption rate \((f = 0.1 \text{ ML min}^{-1})\) as a function of the average surface height \(\bar{h} = f \times t\).

linearly with the cluster size: Specifically, they find an effective diffusion barrier for dimer diffusion, which already the monomer barrier \(E_{\text{mon}}\) is approximately twice as high as that corresponding to monomers. Transferring this trend to our \(\text{C}_{60}\) system, we expect a very large energy barrier for dimer diffusion, which correlates the heights of neighbouring sites. There-fore, we expect cluster diffusion to take place only on very long time scales and, therefore, we expect very little influence of consorted clustering in our system. Thus, we expect cluster diffusion in the dynamical properties studied here.

The simulation parameters are chosen in accordance with recent experiment, in which \(\text{in situ}\) measurements were made during growth. These experiments use x-ray scattering to gain insight into the real-time evolution of both the island density and layer coverage, si-multaneously. The layer coverage is monitored through the modulation of the scattering intensity at the so-called “anti-Bragg point”, while the island density is derived from small-angle x-ray scattering. By comparing these experimentally obtained quantities to corresponding KMC results for a range of temperatures and adsorption rates, we were able to find a consistent set of energy barriers. These are \(E_{\text{free}} = 0.54 \pm 0.04\text{ eV}, E_{n} = 0.13 \pm 0.02\text{ eV}\) and \(E_{\text{ES}} = 0.11 \pm 0.02\text{ eV}\). These parameters have been shown to describe \(\text{C}_{60}\) for the temperature range \(40^\circ\text{C} - 80^\circ\text{C}\) and adsorption rates in the range \((0.1 \text{ ML min}^{-1} - 1 \text{ ML min}^{-1})\), where ML stands for monolayer. We also note that our values are in agreement with previous simulations of a monolayer of \(\text{C}_{60}\) on \(\text{C}_{60}\) if modeling differences (concerning our coarse-graining of the lattice, as well as differences of the definitions of \(E_{n}\) and \(\nu\)) are taken into account. For a more detailed discussion see Appendix A. In the present study we focus on the temperature \(T = 40^\circ\text{C}\).

To demonstrate the quantitative agreement between experiment and KMC simulation, we show in Fig. the experimental and simulated data for the island density as a function of time. Note that, in the experiment, the first layer of \(\text{C}_{60}\) was grown on mica, while our simulation begins on the first closed layer of \(\text{C}_{60}\). Whenever we refer to the first (second, etc.) layer from this point onward we mean the first layer of \(\text{C}_{60}\) on \(\text{C}_{60}\), which is equivalent to the second experimental layer.

### B. Target quantities

The focal point of our study is to explore the interplay between the time-dependent surface morphology, on the one hand, and the particle-resolved dynamics, on the other hand.

To characterize the surface morphology, we calculate the height-height correlation function \(G(d, t)\) defined as

\[
G(d, t) = \left\langle \frac{\sum_{i}^{M} \sum_{j}^{M} (h(x_{i}, t) - \bar{h})(h(x_{j}, t) - \bar{h})}{N(d)} \right\rangle,
\]

(4)

where \(M\) is the number of points on the surface, and \(d = |x_{i} - x_{j}|\) is the distance between two points on the surface, \(i\) and \(j\). These points are characterized by their position vectors \(x_{i}, x_{j}\) and their heights \(h(x_{i}), h(x_{j})\). The function \(G(d, t)\) is determined by averaging over the \(N(d)\) pairs of points on the surface, which have a distance \(d\), followed by an average over realizations (denoted as \(\langle \ldots \rangle\)). In Eq. (4), \(\bar{h}\) is the average height of the surface.

The height-height correlation function \(G(d, t)\) has successfully been used to characterize a variety of systems, both in experimental studies (e.g., in STM-imaging of \(\text{C}_{60}\)) and in simulations. The definition (4) implies two particularly interesting special cases regarding the values of the distance \(d\). The first one corresponds to \(d = 0\) (and thus \(i = j\)). In this case, \(G(0, t)\) can be interpreted as the variance,

\[
G(0, t) = \left\langle \frac{\sum_{i}^{M} (h(x_{i}, t) - \bar{h})(h(x_{i}, t) - \bar{h})}{N(0)} \right\rangle.
\]

(5)

Clearly, the variance is sensitive to deviations from the average surface height \(\bar{h}\), which is why it is commonly interpreted as the roughness. The second special case is that the points \(i, j\) are nearest neighbours \((i, j \in n, \text{which is equivalent to } |x_{i} - x_{j}| = a)\). Then, we find a measure for the mean squared step height,

\[
G(1, t) = \left\langle \frac{\sum_{i,j \in n} (h(x_{i}, t) - \bar{h})(h(x_{j}, t) - \bar{h})}{N(1)} \right\rangle,
\]

(6)

which correlates the heights of neighbouring sites. Therefore, \(G(1, t)\) is the correlation function that is most sensitive to local variations; hence it is often called the local roughness or mean square step height.

A characteristic feature of the present growth process is the formation of islands. As soon as these are present, the surface can also be characterized through scalar morphological descriptors such as the fractal dimension \(D\).
The latter is determined through the scaling behavior of island surface \( A \) with the radius of gyration \( x_{\text{gyr}} \)

\[
A \propto x_{\text{gyr}}^D,
\]

where \( x_{\text{gyr}} \) is defined as

\[
x_{\text{gyr}} = \sqrt{\frac{1}{N_{\text{island}}} \sum_{i \in \text{island}} (x_i - \bar{x}_{\text{island}})^2}. \tag{8}
\]

In Eq. (8), \( N_{\text{island}} \) is the number of particles in the island, and \( \bar{x}_{\text{island}} \) is the center-of-mass position of the island, i.e.

\[
\bar{x}_{\text{island}} = \frac{1}{N_{\text{island}}} \sum_{i \in \text{island}} x_i. \tag{9}
\]

The island is defined using a cluster algorithm (Hoshen-Kopelman algorithm, see \cite{53}) to identify all particles within one island.

The fractal dimension \( D \) describes how branched structures are: the closer to two the fractal dimension of a 2D island is, the less dendritic is its morphology. Because the island size increases in discrete steps, the scaling behavior of \( A \) [see Eq. (7)] breaks down for small islands. So far we have focused on system-averaged quantities. To understand the dynamics on a particle level, we analyze the mean-squared displacement (MSD) of particles as a function of time. As the particle dynamics depend on the morphology of the substrate, only particles that arrive on the surface at time \( t \) after beginning of surface growth are considered in the average over realizations (e.g. after the growth of 0.5ML). We then define the MSD as

\[
\Delta x(t^*)^2 = \langle (x(t^*) - x(0))^2 \rangle_t,
\]

where \( x(t^*) \) is the position of the particle at the time \( t^* \) after it’s arrival on the substrate, and \( \langle \ldots \rangle_t \) is the average over all realizations for particles that arrive at time \( t \). For free diffusion the MSD scales linearly in time, while for immobile particles it assumes a constant value. If the MSD scales slower (faster) than linearly with \( t \), the behavior of the island size increases in discrete steps, the scaling behavior of \( A \) [see Eq. (7)] breaks down for small islands.

To interpret our MSD results, we look at the processes occurring at time \( t^* \). The process types considered are free diffusion, diffusion away from sites with neighbouring particles, diffusion across step edges and also immobilization. Immobilized particles are embedded and remain immobilized for the rest of the simulation. We define \( N(p, t^*) \) as the fraction of particles that perform a specific process of type \( p \) at time \( t^* \).

\section{Systems under investigation}

A focal point of our study is to contrast the growth dynamics of C\textsubscript{60} against representative atomic systems. For the latter, we choose Pt grown on Pt(111) and Ag grown on Ag(111). For C\textsubscript{60}, the energetic barrier stemming from the interactions with the nearest neighbours is relatively small; an effect which we explain through the fact that the attractive center-of-mass interactions between two C\textsubscript{60} molecules have a rather short range (as compared to atomic systems). As a consequence, the ratio between the energy barrier for in-plane diffusion, on the one hand, and the total energy barrier for a particle to break from a dimer, \( E_n + E_{\text{free}} \), on the other hand, is relatively large. Specifically, we find (see Table I)

\[
R(C_{60}) = \frac{E_{\text{free}}}{E_{\text{free}} + E_n} \approx 0.8. \tag{11}
\]

This large value of \( R \) is the major effect of the size of C\textsubscript{60} and its small interaction range on the energy parameters \( E_{\text{free}}, E_n \) and \( E_{\text{ES}} \). To isolate, within our KMC simulations, the role of neighbour interactions on the growth of representative atomic systems relative to C\textsubscript{60} growth, we proceed as follows: The atom-like KMC simulations are performed with the same values of \( E_{\text{free}}, E_{\text{ES}} \) used in the C\textsubscript{60} simulations, as well as with the same lattice configuration and experimental input parameters. However, the values for the neighbour interaction \( E_n \) of atomic systems are chosen such that the ratio \( R = E_{\text{free}}/(E_{\text{free}} + E_n) \) fulfills the literature values of \( R \approx 0.37 \) for Pt and \( R \approx 0.43 \) for Ag. The values used in determining these ratios are listed in Table I and discussed in Appendix B.

Analyzing systems that are identical in all parameters except the ratio \( R \) allows us a direct comparison of single-particle dynamics despite the smaller time- and length scales of growth in atomic systems relative to C\textsubscript{60}.

\section{RESULTS}

\subsection{Morphology and trajectories}

To start with, we show in Fig. 2 two surface structures illustrating the morphology of C\textsubscript{60} and the Ag system after the growth of 1.5 ML. The adsorption rate here and in the following figures is \( f = 0.1 \) ML min\textsuperscript{-1}. All lengths are plotted in units of the lattice constant, \( a \). It is seen that the depicted surfaces have distinctly different structures. Most prominently, C\textsubscript{60} has well rounded islands while Ag forms dendritic, nearly fractal structures. This morphological difference reflects the fact that C\textsubscript{60} has a noticeably higher ratio \( R \) than Ag [see Eq. (11)]; therefore, processes that break bonds to lateral neighbours...
FIG. 2. (color online) Height of surface structures after the growth of 1.5 ML for (a) C$_{60}$ on C$_{60}$(111) and (b) Ag on Ag(111). The black lines depict trajectories of a particle which arrived on an island. Both systems are simulated on a triangular lattice with equal energy barriers $E_{\text{free}} = 0.54$ eV and $E_{\text{ES}} = 0.11$ eV, but different neighbour binding energies $E_{n} = 0.13$ eV and $E_{n}(\text{Ag}) = 0.72$ eV, respectively.

are far more likely. As a consequence, particles can easily move to sites with high coordination numbers, which then again results in rounded islands. On the contrary, Ag is characterized by a much smaller ratio $R$. Therefore, once particles are bound to their neighbours these bonds are less likely to break. As a result one observes the formation of dendritic structures.

In Figs. 2(a) and (b) we have included a typical single-particle trajectory illustrating the individual motion of that particle after arrival on an island. For both systems, we clearly see that motion across a step edge is hindered. This leaves the particles to meander mainly on the island surface, caged through the island edges. However, as Figs. 2(a) and (b) clearly show, the different shapes of the islands influence the shape of the paths. In particular, the rounded islands of C$_{60}$ lead to caging into a relatively small surface area within which the particles can diffuse essentially freely. On the other hand, the more fractal structure of the islands formed by Ag allows for longer paths of free diffusion (“stretches”), that is, particles move along “channels” formed by island edges.

B. Correlation functions

In the previous paragraph we have seen that the local dynamics depends crucially on the morphology of the surface. Thus it is important to understand the evolution of the surface morphology with time. To this end, we now discuss the behavior of the spatio-temporal correlation functions introduced in Eqs. (4)-(6).

To start with, Fig. 3(a) depicts the height-height correlation function $G(d,t)$, which correlates the deviation from the average height $\bar{h}$ at two points with distance $d$ at time $t$ [see Eq. (4)]. Specifically, we focus on a time during the growth of the first monolayer ($t \approx 22$ s). For the Ag system, $G(d,t)$ decays rapidly to zero. The corresponding function for C$_{60}$ reflects correlations ranging over much larger distances. These differences can be understood using the surface snapshots shown in the inset of Fig. 3(a). The C$_{60}$ system displays clearly separated islands with well defined radii and distances. These features are mirrored by strong and long-ranged spatial correlations in the corresponding $G(d,t)$. In particular, the maximum at $42 \, \text{a}$ corresponds to the average distance between neighbouring islands. The Ag system, however, is characterized by a far more dendritic island structure, which is reflected by the short range and smooth structure of $G(d,t)$.

The different island structures of C$_{60}$ and Ag can be quantified through the fractal dimension $D$. We have de-
determined this quantity via a scaling plot of the island area as function of the radius of gyration (see Fig. 3(b) and Eq. (7), respectively). From this we find $D \approx 1.84$ for C$_{60}$ and $D \approx 1.41$ for Ag. The much smaller values for Ag indicates the dendritic morphology of Ag islands. This confirms our interpretation that the small value of $D_{\text{Ag}}$ is due to its strongly dendritic growth. Regarding the fractal dimension for C$_{60}$, we note that despite the rather large, “colloid-like” value of the energy ratio $R$, our value of $D$ deviates from the fractal dimension characteristically found for (uncharged) colloidal systems.$^{62,63}$ Rather it lies within the range of values expected for atomic systems.

To further characterize the growth, we show in Fig. 4 the correlation functions $G(0, t)$ of C$_{60}$ and Ag as a function of time for two distances (a) $d = 0 \alpha$, (b) $d = 1 \alpha$.

![FIG. 4. (color online) Height-height correlation functions $G(d, t)$ of C$_{60}$ and Ag as a function of time for two distances (a) $d = 0 \alpha$, (b) $d = 1 \alpha$.](image)

The first layers ($t \lesssim 200$ s), C$_{60}$ and Ag grow with an identical roughness $G(0, t)$, indicating that the systems do not differ significantly in their inter-layer diffusion behavior and follow similar growth modes. In the subsequent time range $200 \lesssim t \lesssim 400$ s, Ag maintains a constant roughness with a value of about 0.2, while the roughness of C$_{60}$ progressively increases. We interpret the behavior of Ag as prolongation of layer-by-layer growth (which is characterized by approximately constant deviations of local from average surface height). Since the Ag system is simulated with the same Ehrlich-Schwoebel barrier as the C$_{60}$ system, the observed deviation in the temporal behavior of the roughness indicates a complex coupling of particle trajectories and surface morphology. Finally, for long times ($t \gtrsim 1000$ s), the roughness of Ag and C$_{60}$ increases with the same exponent, though the curves are shifted with respect to each other due to the different behavior at intermediate times.

More pronounced differences are seen in the local roughness $G(1, t)$, plotted in Fig. 4(b). This is expected, since $G(1, t)$ is more sensitive to the differences in surface morphology seen in Figs. 2 and 3. One main feature of the C$_{60}$ growth is the rounded island structure. This leads to a slower increase of the local roughness compared to the Ag system, where the islands are dendritic. On the other hand, the Ag system is characterized by a layer-by-layer-like growth at intermediate times. This is reflected by the longer plateau on the corresponding $G(1, t)$ in the corresponding range of times. However, for long times the local roughness of C$_{60}$ grows faster than for Ag, resulting in very similar values of $G(1, t)$ at long times. This can be interpreted as an indication for similar morphologies in the two systems during the late stages of growth.

### C. Local Dynamics

We now turn to the dynamics on the particle-resolved level. Figure 5 depicts the MSD after the growth of 0.5 ML where we differ between particles that arrive in between [Fig. 5(a)] and on [Fig. 5(b)] islands. All curves share the same general structure in that the MSD initially grows in time (with exponent $\approx 1$) and then saturates, indicating immobilization. However, when comparing the curves for arrivals in between and on islands, the two systems behave differently. Indeed, the diffusion behavior of the Ag system is quite sensitive to the location of a particle’s arrival, whereas that of C$_{60}$ is not. We now relate these features to the morphology.

In the atomic system, the islands are fairly dendritic [see Fig. 2(b)]. As a consequence, particles that arrive in between the islands [Fig. 5(a)] travel only small distances before they encounter the edge of an island. In this situation the majority of atomic particles either attaches for long time spans or becomes immobilized completely,
as further particles attach before they can detach themselves. This leads to an early onset of sub-diffusive behavior (for $t^* > 0.05 \text{ ms}$) and average travel distances of just a few nanometres before the particles are immobilized (see plateau in the MSD).

A quite different behavior is seen for atomic particles that arrive on the islands [see Fig. 5(b)]. These particles can diffuse across fairly large dendritic structures before encountering other particles. The step edges hinder particles from leaving the island, but they do not really slow down their motion on the islands. Therefore, atomic particles on the islands can travel significantly further (as compared to the case discussed before) before they become immobilized and the MSD saturates.

The C$_{60}$ system is characterized by a completely different island morphology [see Fig. 2(a)]. As a consequence, molecules that arrive between islands can diffuse far longer distances before encountering other molecules, just because there is more free space. Moreover, C$_{60}$ molecules can detach after encountering other molecules (as a result of the weaker binding). These effects lead to much larger traveled distances both between and on islands. Furthermore, the MSD curves for these two cases are rather similar.

An even better understanding of the systems emerges when we relate the MSDs to the occurrence of certain individual processes. This is done in Fig. 6 where we focus on particles arriving in between islands. Parts (a) and (c) show the corresponding MSDs, while parts (b) and (d) contain data for the fraction of particles involved in a specific process, $N(p, t)$. For both, C$_{60}$ and Ag systems it is clearly visible that at early times (i.e. before the majority of particles interact with other particles) the main contribution to the MSD stems from freely diffusing particles ($n = 0$). However, once particles begin to interact, distinct differences between C$_{60}$ and Ag become apparent. During the growth of C$_{60}$ there are many events where particles detach from one or two neighbouring particles (see curves in Fig. 6(b) with $n = 1, 2$). Such events are absent in the Ag system. We understand this difference as a consequence of the larger binding energy in the Ag system.

**IV. CONCLUSION**

In this paper we have discussed the local and global dynamics accompanying the surface growth of the nanomolecular system C$_{60}$. One main goal in this context was to understand the similarities and differences between nanomolecular and atomic growth for the spherical molecule C$_{60}$. To this end, we have identified energetic differences between the two system types and used these to study both, single-particle trajectories and the overall surface morphology.

We have found that there are indeed pronounced differences in the surface morphology during growth: The C$_{60}$ system displays compact islands with a rather large fractal dimension and significant spatial correlations between the islands. In contrast, the fractal dimension and range of ordering are far smaller in atomic systems. These differences in the global surface morphology during growth can be traced back to the differences in the energy barriers that single particles have to overcome. Moreover, we have shown that the differences in morphology is intimately related to the single-particle dynamics. Atomic particles diffusing between islands can cover only small distances before they are immobilized, because the islands are fairly dendritic. On the other hand, particles in the C$_{60}$ system can diffuse quite far, since the compact islands are separated through large, free surfaces.

The large diffusion distances are effectively even enhanced by the fact that due to the small binding energies, C$_{60}$ molecules can detach from island edges before they are immobilized. However, unlike colloidal systems, C$_{60}$ has to overcome an energetic atom-like step-edge barrier for interlayer diffusion. This leads to a reduced mobility of both, molecules and atoms, between layers, leading to a roughening of the surface on large time-scales.

In summary we find a complex interplay of local and global dynamics, whose characteristics reflect special molecular features of C$_{60}$, in particular the relatively small effective binding energy. Starting from our findings, one interesting question for further studies would be the connection between single-particle-trajectories and the long-time scaling behavior resulting from continuous rate-model descriptions.

Further, for a more detailed insight concerning the interplay of energy landscape and the dynamics, it may be interesting to couple KMC simulations and MD simulations. Withing such a study, configurations gained from KMC could be used to initialize MD simulations. Reversely, the MD simulations could be used calculate...
FIG. 6. (color online) Part (a) and (c) show the MSD of the C\textsubscript{60} and Ag systems already plotted in Fig. 5 (a) (i.e. diffusion in between islands), while (b) and (d) correlate these data to the time dependence of the fraction of particles doing a certain process. These processes can be free diffusion ($n = 0$) and diffusing away from a site with $n = 1$ or 2 neighbour particles. Also plotted are the fractions of particles that are immobilized (bound). All other processes are negligible.

the fly” the energy parameters required in the KMC simulations, thus taking into account the time-dependence of the energetics. Such an approach would yield important insight into all time-scales from up to $O(10^{-9})$s towards $O(10^4)$s.

Experimentally, real-time measurements of the surface morphology during the growth of organic molecules are possible through x-ray scattering\cite{10} or low energy electron microscopy\cite{12,13}. Particle-resolved dynamical quantities are harder to access in experiment because of the time-scales involved. However, if the dynamics is slowed down through cooling, scanning tunneling microscopy could be used to track the motion of individual molecules on a substrate and to determine waiting times in each potential well\cite{68}. This may open the path to experimentally observe quantities such as the ones obtained in the present work, similar to what has been done in colloidal surface growth\cite{67}.

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Appendix A: Comparing C\textsubscript{60} energy parameters to literature

The energy parameters listed in Table I are of the same order of magnitude as other values reported in the literature, but differ in their actual magnitude. In the following we briefly discuss to which end these differences can be attributed to differences of energy barrier definitions and of simulation approaches. We start by considering the energy barrier stemming from nearest-neighbour interactions. The corresponding value quoted in the KMC study of Körner et al.\textsuperscript{64} is $E_{\text{Körner}} = 0.271 \text{ eV}$. This equals the depth of the pair interaction potential of two interacting C\textsubscript{60} molecules, as derived by Girifalco\textsuperscript{65}. However, particles in the simulation of Körner et al. need to overcome $nE_{\text{b}}/2$ to move from a site with $n$ neighbouring particles to a site with no neighbouring particles. Therefore the definition of $E_{\text{b}}$ differs from our definition of $E_{\text{n}}$. To be correct, we have to compare $E_{\text{Körner}}/2 = 0.1355 \text{ eV}$ with our value $E_{\text{n}} = 0.13 \pm 0.02 \text{ eV}$. Clearly, these are in very good agreement.

Next, we consider the free diffusion energy. Both Körner et al.\textsuperscript{64} and Liu et al.\textsuperscript{61} report a value $E_{\text{free, Körner}} = 0.178 \text{ eV}$; however, they also use an attempt frequency of $\nu = 2 \cdot 10^{11} \text{ Hz}$. Moreover, both studies are based on a hexagonal lattice under consideration of interstitial sites. Here, we neglect these sites, yielding a somewhat coarse-grained approach. We note that without the coarse-grained approach it would not be possible to simulate such a large system for minutes to hours of experimental time. In one diffusion step on our coarse-grained lattice a particle overcomes two times the barrier $E_{\text{free, Körner}} = 0.178 \text{ eV}$. In addition there three options to diffuse from the interstitial site. Since only one option leads to our coarse-grained destination site, an additional geometric factor of $1/3$ needs to be included in the diffusion rate.

Taking, furthermore, the difference in the attempt frequency $\nu$ into account, we gain the following estimate of a coarse-grained free diffusion barrier from the values reported in\textsuperscript{63,64}

$$ E_{\text{free, Körner}} \approx -\ln \left( \frac{1.4 \cdot 10^{13} \text{ Hz}}{2 \cdot 10^{11} \text{ Hz}} \right) kT - \ln \left( \frac{1}{3} \right) kT $$

$$ + 2 \cdot E_{\text{free, Körner}} $$

$$ \approx 0.122 \text{ eV} + 0.032 \text{ eV} + 0.356 \text{ eV} \approx 0.51 \text{ eV}, \quad (A1) $$

which lies within the error margins of our value $E_{\text{free}}$ (see Table I). This estimate was gained using $T = 60^\circ \text{C}$.

Finally, our value of the Ehrlich-Schwoebel barrier $E_{\text{ES}}$ is in very good agreement with values derived from density-functional theory calculations for step edge barriers $E_{\text{ES}} \approx 0.104 \text{ eV}$\textsuperscript{66}.

Appendix B: Comparison between C\textsubscript{60} and atomic systems

The comparison to atomic systems considered in this work is made possible through the work of other groups, in which the energy parameters listed in Table I were successfully employed to simulate atomic growth on a coarse-grained lattice such ours.

Pt on Pt(111)

Hohage \textit{et al.}\textsuperscript{61} used a free diffusion energy of $E_{\text{free, Pt}} = 0.26 \text{ eV}$ and a attempt frequency of $\nu = 5 \cdot 10^{12} \text{ Hz}$ to simulate the growth of Pt on Pt(111). They employed a simulation grid that only contains sites that are occupied in a bulk crystal. This approach to lattice coarse-graining is equivalent to ours, which enables a comparison between diffusion energies. Specifically, we compare the energy $E_{\text{free, Pt}}$ to the free diffusion energy $E_{\text{free}}$ of C\textsubscript{60}, where $E_{\text{free, Pt}}$ is related to $E_{\text{free, Pt}}$ via the attempt frequency

$$ E_{\text{free, Pt}} = 0.26 \text{ eV} - \ln \left( \frac{5 \cdot 10^{12} \text{ Hz}}{1.4 \cdot 10^{13} \text{ Hz}} \right) kT \approx 0.29 \text{ eV}. \quad (B1) $$

Comparing this value to neighbour interaction energies mentioned in the study by Feibelman and Michely\textsuperscript{63}, who found $E_{\text{b,2}} = 0.5 \text{ eV}$, we obtain a ratio

$$ R(\text{Pt}) = \frac{E_{\text{free, Pt}}}{E_{\text{free, Pt}} + E_{\text{b,2}}} \approx 0.37. \quad (B2) $$

Ag on Ag(111)

The values for free diffusion energy barriers for Ag/Ag(111) reported in the literature show a wider spread, presumably due to the tendency of Ag to oxidize and the influence of this impurity on measurements. Values quoted range from $E_{\text{free, Ag}} = 0.1 \text{ eV}$ with $\nu = 10^{11} \text{ Hz}$\textsuperscript{68} and $E_{\text{free, Ag}} = 0.097 \text{ eV}$ with $\nu = 2 \cdot 10^{11} \text{ Hz}$\textsuperscript{69}.
via the combination of $E_{\text{free,Ag}} \approx 0.067\,\text{eV}$ with $\nu = 10^{12}\,\text{Hz}$ to $E_{\text{free,Ag}} = 0.1\,\text{eV}$ with $\nu = 10^{13}\,\text{Hz}$ and the combination of $E_{\text{free,Ag}} = 0.12\,\text{eV}$ with $\nu = 10^{13}\,\text{Hz}$. All of the quoted values have been used to study Ag on Ag(111) using kinetic Monte-Carlo simulations on a coarse-grained lattice.

In view of this spread, we have considered an intermediate value for the diffusion energy-barrier, which was determined for pure Ag using Molecular Dynamics and nudged-elastic band approaches:

$$E_{\text{free,Ag}} = 0.067\,\text{eV} - \ln\left(\frac{10^{12}\,\text{Hz}}{1.4 \cdot 10^{13}\,\text{Hz}}\right) kT \approx 0.143\,\text{eV}.$$  \hspace{1cm} (B3)

Similarly the range of neighbour interaction energies ranges from $E_n = 0.15\,\text{eV}$ to $E_n = 0.24\,\text{eV}$ (and references within), while most studies appear to agree on $E_n \approx 0.19\,\text{eV}$. Using these values we find:

$$R(\text{Ag}) = \frac{E_{\text{free,Ag}}}{E_{\text{free,Ag}} + E_n} \approx 0.43.$$  \hspace{1cm} (B4)