Predicting patterns for molecular self-organization on surfaces using interaction-site models

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I. INTRODUCTION

Molecular building blocks interacting at the nanoscale organize spontaneously into stable monolayers [1]. The patterns that emerge upon self-organization of simple supramolecular units display a variety of symmetries and local ordering motifs with different degrees of packing on the surface. Currently such surface coatings are under active research due to their potential applications in nanoscience, such as surface functionalization [2], sensor surfaces [3], or molecular electronics [3]. The theoretical challenge is to provide tools that allow to predict the patterns without performing the actual measurements for the supramolecular units [2]. Most approaches rely on atomistic modeling where the stable conformations are calculated using experimental measurements of the molecular conformations on the surface as input. There, the molecular subunit is resolved in all chemical details, resulting in a large number of degrees of freedom that have to be included in the modeling. In molecular mechanics calculations (MM) [6] and molecular dynamics simulations (MD) [7, 8] the molecular interactions are parametrized by semi-empirical force fields which requires a significant number of additional parameters. In MM the starting conformations are energy-minimized resulting in a stable configuration, yet the method intrinsically provides only the closest local minimum. In contrast, MD simulations sample different minima and incorporate, in principle, also dynamical reconfigurational processes. The quantum aspects such as the electronic density of states (DOS) measurable in scanning tunneling microscopy (STM) can be computed using density functional theory (DFT) [8, 9], yet these calculations are limited to small systems.

Recently, a complementary approach has been introduced employing coarse-grained models which aim at predicting certain features of the patterns with the benefit of a great reduction of complexity. For example, using an effective hamiltonian accounting for the energetics of the respective orientations of neighboring molecules, local ordering motifs for oligopyridine supramolecules on a surface have been successfully reproduced [10]. For mixtures of melamines, PTCDI, and PTCDA structural stability diagrams of two competing patterns have been reported [11, 12] using effective pair energies between neighboring molecules on a lattice. For the case of flexible organic molecules, we have recently shown that a multi-method approach combining MM, DFT, and Monte Carlo simulations is capable of providing reliable predictions for the emerging multiple coexisting patterns on surfaces [13, 14].

In this paper we provide a detailed discussion of the theoretical aspects of the use of interaction-site models for Fréchet dendrons. In particular, we discuss how salient features of the molecular structure can be identified and used to tailor a suitable coarse-grained model and then be studied by means of Monte-Carlo methods. Furthermore, we show that a phase diversity naturally emerges in agreement with experimental studies and discuss the corresponding phase stability as the packing fraction on the substrate or the temperature is varied. Then we provide a thorough discussion on the merits of the approach and its limitations as well as possible extensions.
II. EXPERIMENTALLY OBSERVED PATTERNS

In this Section we first summarize the experimental findings on molecular self-organization for Fréchet dendrons [16,17]. These second generation Fréchet dendrons are flexible supramolecules, which consist of three phenyl rings symmetrically disposed at the vertices of a triangle with two alkoxychains attached at each lateral phenyl ring. The arms of these chains consist at one side of the molecule of twelve carbon atoms, and on the other side of eight carbon atoms—see the structural formula in Fig. 1.

Figure 1: Stick model of the asymmetric Fréchet dendron used in the experiments.

Scanning tunneling microscopy (STM) images show that a large variety of self-organized ordering motifs on top of highly oriented pyrolytic graphite (HOPG) emerges [18,19]. This substrate exhibits a honeycomb-like surface with a six-fold rotational symmetry. Seven general ordering motifs have been reported, five of which are flat-lying configurations [13]. The tiretrack, wave, honeycomb, sawtooth, and jigsaw motifs are displayed in Fig. 2. These patterns coexist on the HOPG surface and phase transform over time into the thermodynamically stable tiretrack pattern. The schematics of the ordering motifs, Fig. 2, have been obtained employing atomistic modeling by molecular mechanics energy minimizations using the Forcite module of Materials studio 4.3 and employing a universal force field.

III. THE INTERACTION-SITE MODEL

To obtain reliable predictions of the emergent pattern in the assembly of monolayers without any a priori knowledge from the experiments, a drastic reduction of complexity is highly desirable. Here, we propose an interaction-site model which aims to provide a suitable description of the self-organization process. The basic idea is to reduce the numerous microscopic forces to a few representative interactions acting on groups of selected points. The major challenge consists of appropriately identifying the positions of the interaction centers and forces relevant for the self-organization. We will demonstrate in this paper that the geometry of the building blocks, the symmetry of the substrate, and the coupling of both are key elements in the self-organization of monolayers. We will show for an experimental model based on Fréchet dendrons, that the interaction-site model properly captures the essence of the system, predicts the observed patterns, as well as the temperature regime at which they are stable. Moreover, monitoring suitable order parameters, we are able to identify in principle the nature and location of the melting transition.

A. Construction of the interaction sites

The Fréchet dendron introduced above is a suitable and especially versatile model system to assess the validity of an interaction-site approach in the prediction of self-organized monolayers. According to the experimental observations the crucial features leading to the self-organization are the steric repulsion between the molecular rings, the weak interactions of the carbonated chains, as well as the coupling of the building blocks with the
substrate. We model the symmetric molecular core as three hard spheres of radii \( r_r \), located at the vertices of a flattened isosceles triangle—large spheres in the sketch of Fig. 3. The long base of the triangle is twice of its height \( l \), hence all three interaction sites have equal distance \( l \) from the center of the base. The carbonated chains of the molecules are modeled by a small number of sites with Lennard-Jones interactions. Four neighboring CH\(_2\) units of the alkoxychain are coarse-grained to one Lennard-Jones site—small spheres in Fig. 3. The interaction sites are arranged in straight, rigid arms with their centers separated by a distance \( \sigma \).

The radii of the hard spheres and the range of Lennard-Jones interaction, the distance of the former to the molecular center, as well as the length and orientation of the arms are the parameters of the model. These geometrical features are obtained from the conformations which minimize molecular mechanics simulations (MM) starting from an initial configuration derived from a detailed analysis of the experimental STM images, Fig. 2. The relevant length scales of the Fréchet dendrons range approximately from 15 Å of the skeleton to 50 Å for the extended molecule, with \( l = 6.1 \text{ Å} \), \( r_r = 2.6 \text{ Å} \) and \( \sigma = 6 \text{ Å} \).

![Figure 3: Interaction-site model for a Fréchet dendron in conformation \( \alpha \). Large spheres account for aromatic rings, whereas the small spheres represent subunits in the carbonated chains. Every sphere represents four CH\(_2\) units in the arms of the dendrons.](image)

We encode the strong intermolecular steric interaction between the aromatic rings by hard-sphere repulsions between the three central spheres of different molecules, preventing the cores of the molecules from overlapping. The weak, short-ranged van-der-Waals attraction of the lateral chains is described by a Lennard–Jones potential: \( V(r) = 4 \epsilon \left[ (\sigma/r)^{12} - (\sigma/r)^{6} \right] \) among beads in chains of different molecules. Thus \( \epsilon \) corresponds to the minimum energy which occurs at \( r = 2^{1/6} \sigma \).

The atomically flat graphite surface which constitutes the template for the pattern formation, offers six energetically equivalent orientations for the molecule. The molecule-substrate attraction is mainly mediated by \( \pi \)-interactions between the phenyl-rings and the chains with the graphite surface, and the total adsorption energy is about ten times larger than the total intermolecular interaction. In addition, as the size of the entire molecule, around 45 Å, is up to ten times larger than the lattice constant (a few Å), only the symmetry of the underlying substrate plays a role in the monolayer assembly.

In our modeling the molecules are fixed at the sites of a coarse-grained, fully occupied triangular lattice. The lattice constant \( a \) is comparable to the size of the building blocks and the lattice exhibits the same symmetry as the original graphite honeycomb structure. The Fréchet dendrons may rotate by discrete angles as rigid bodies around their centers and adopt one of the six preferred orientations of the underlying graphite.

The interaction-site model accomplishes a significant reduction of degrees of freedom, setting the flexibility of the molecule aside. While the actual physical system contains hundreds of atoms per molecule able to displace and rotate independently, the coarse-grained interaction-site model consists of a rigid object with no other degrees of freedom than the rotation around its center.

In addition to the conformation closest to the experimental findings, Fig. 3, we explore the Fréchet dendron in five alternative conformations by varying the orientations of the arms, as displayed in Fig. 4 where the angles follow the symmetry directions of the substrate.

![Figure 4: Molecular conformations showing different orientations of the lateral straight arms. The angles of the arms with respect to the positive \( x \)-axis are given clockwise from the left to the right for the five additional conformations: \( \beta = (−5\pi/6, 5\pi/6, 5\pi/6, −\pi/6, −\pi/6) \), \( \gamma = (−5\pi/6, \pi/2, \pi/2, −\pi/6, −\pi/6) \), \( \delta = (−5\pi/6, \pi/6, \pi/2, \pi/6, \pi/6) \), \( \epsilon = (−5\pi/6, \pi/2, \pi/2, \pi/6, \pi/6) \), \( \zeta = (−5\pi/6, \pi/6, \pi/6, −\pi/6, −\pi/6) \).](image)

**B. Predictions of the model**

To find the regular patterns emerging in the self-organized monolayers we have run Monte Carlo (MC) simulations considering some hundred to a few thousand molecules which corresponds also to the experimental situation: a single dendron covers a surface of approximately 4 nm\(^2\) and the samples imaged with STM...
occupy some hundred nm$^2$. The lattice constant which essentially fixes the packing fraction of the monolayer has been varied from $a = 2.8 \sigma$ to $a = 4.2 \sigma$ covering the experimental regime. To ensure that the stable patterns are assumed in the simulations, simulated annealing has been employed. Random configurations, where molecules assume a random direction among the six possible orientations, have been chosen as initial configurations. Starting at a given temperature the system evolves via Monte Carlo moves by performing $\pi/3$ rotations. We have run 500 MC sweeps to equilibrate the sample and measure the energy and order parameters during another 1000 Monte Carlo sweeps before lowering or raising the temperature. Then the temperature is lowered and the process is repeated. The system is cooled down to temperatures around 170 K, low enough for our purpose, given that the experiments were performed at room temperature.

![Image of patterns](image)

Figure 5: Ordered motifs found by simulated annealing for the Fréchet dendrons with different conformations within the interaction-site model. Molecules are represented as wedges matching their three aromatic rings. The carbonated arms are omitted for clarity.

An abundant variety of ordered patterns arises by cooling samples of the interaction-site model in all conformations, see Fig. 4. These patterns display different degrees of symmetries which are subgroups of the $p6m$ symmetry (six-fold rotation, mirror symmetry) of the underlying lattice mimicking the graphite substrate. The honeycomb, trimer and inverted honeycomb structure, see Fig. 4 display a $p6$ symmetry, i.e. the sixfold rotational symmetry is still present, yet the mirror symmetry of the substrate is broken. The sawtooth pattern exhibits only a $p3$ with threefold rotations of the unit cell. In the tiretrack/wave pattern rows of aligned units emerge with opposite directions resulting in a $p2gg$ symmetry, i.e. a twofold rotational symmetry and glide-mirror axes. The class of $p2$ symmetric patterns consists of the jigsaw, zipper and rhomboid ordering. Here the jigsaw unit cell is comprised only of two units arranged in a head-to-head configuration, whereas the more exotic zipper contains four molecules in a unit cell, the rhomboid pattern even six building blocks. The lowest symmetry $cmn$ consisting of a mirror axis and a glide mirror axis, yet no rotational symmetry, is realized in the crown pattern, where four molecules order in a head-in fashion.

Table I lists the patterns found in the cooling process for the different conformations. Some patterns turn out to be only metastable and the ground state may change upon varying the packing fraction. The configuration $\alpha$ which resembles most closely the experimental configuration displays a significantly larger variety of patterns.

To assess the stability of the emergent patterns, we have prepared perfectly ordered configurations at low temperatures and heated them up slowly while monitoring the evolution of the energy and suitable order parameters. Thus, one can identify metastable phases which directly transform into a disordered state. In particular, one can estimate the melting temperature of the broken symmetry phase and determine whether the transition is continuous or discontinuous.

The order parameter is defined explicitly for every pattern, based on the fraction of molecules in a given sublattice following its preferred orientation. Indeed, one can distinguish various sublattices in which the molecules point in the same direction; for instance, alternating rows in the tiretrack/wave pattern represent two different sublattices. Thus, for a sublattice $A$ with $N_A$ molecules and preferred orientation $\sigma^A$, the partial order parameter reads

$$m_A = \frac{N_A^{\sigma^A}}{N_A} - \frac{1}{5} \sum_{\sigma_i \neq \sigma^A} \frac{N_A^{\sigma_i}}{N_A}.$$  

The factor $1/5$ is introduced to ensure that $m_A = 0$ in a disordered phase where all six orientations are equiprobable. The global order parameter we monitor is just the average of the order parameters $m_i$ over all sublattices $n_s$

$$m = \frac{n_s}{\sum_{i=1}^{n_s} m_i}.$$  

The thermal fluctuations of the order parameter encode the linear response of the system with respect to a fictitious external aligning field. Then a susceptibility can be defined as

$$\chi_m = \frac{N}{k_B T} \left( \langle m^2 \rangle - \langle m \rangle^2 \right).$$  

and its behavior as a function of temperature is indicative of the nature of the transition. Similarly, we measure in the Monte Carlo simulation the average energy per molecule $\langle u \rangle$ and the corresponding fluctuations

$$c_N = \frac{N}{k_B T^2} \left( \langle u^2 \rangle - \langle u \rangle^2 \right).$$  


which represents the specific heat per particle.

The simulation results are exemplified in Fig. 6 for the melting transition of the sawtooth phase as a function of the reduced temperature $k_B T/\epsilon$. The average energy and the order parameter drop in a small temperature interval suggesting a first order melting transition. The corresponding susceptibilities exhibit corresponding peaks close to the transition temperature, and are interpreted as smeared delta functions. Yet, we cannot exclude a continuous transition, and finite size scaling would be needed to clarify the order of the transition. In this work we focus on the pattern diversity and have not pursued this issue any further.

### Table I: Emerging ordered phases by cooling down samples with $N = 576$ Fréchet dendrons for the chain conformations $\alpha, \ldots, \zeta$. The phases in bold font are stable under heating, while the other phases would be unstable in an experiment at room temperature.

| Configuration | Patterns                  |
|---------------|---------------------------|
| $\alpha$      | Tiretrack/wave            |
|               | Sawtooth                  |
|               | Jigsaw                    |
|               | Honeycomb                 |
|               | Rhomboid                  |
| $\beta$       | Sawtooth                  |
|               | Tiretrack/wave            |
| $\gamma$      | Tiretrack/wave            |
|               | Honeycomb                 |
|               | inverted Honeycomb        |
| $\delta$      | Trimer Honeycomb          |
| $\epsilon$    | Jigsaw                    |
|               | Trimer Honeycomb          |
|               | Crown                     |
| $\zeta$       | Tiretrack/wave            |
|               | Zipper                    |

Figure 6: Melting transition for the sawtooth phase. Top: Energy and heat capacity per molecule as a function of the dimensionless temperature. Bottom: Order parameter and susceptibility. The simulation was performed for $N = 576$ Fréchet dendrons in the $\beta$ conformation on a lattice with $a/\sigma = 3.8$.

#### C. Comparison to experiments

The interaction-site model reproduces many of the features of the experimental model system consisting of Fréchet dendrons on graphite surfaces. First, in both systems an ample diversity of patterns emerges suggesting that the basic building blocks are correctly transferred from the Molecular Mechanics calculations to the interaction-site model. Furthermore, the patterns found in the theoretical model closely resemble the experimental ones both in its global and local ordering motifs, i.e. the structure displays the same wallpaper group [26] and a similar arrangement of the molecules in a unit cell.

In the highly symmetric trimer honeycomb structure three molecules align in a subunit facing each other. The resulting trimer exhibits a threefold rotational symmetry without additional mirror symmetry implying that the trimer is chiral. These trimers order in sixfold symmetric arrangement where a single molecule of unspecified orientation resides at its center, see Fig. [5]). In the experimental system precisely the same structure has been observed where the center of the hexagons appear as blurred regions in the STM measurements [13]. Thus it appears that these unpaired molecules are free to change their orientation rapidly, much faster than the time resolution of the STM [27].

The tiretrack/wave pattern is characterized by alternating columns of molecules pointing in the same direction. Then in the corresponding rows of this pattern every second molecule possesses the same orientation. Depending on the conformation of the arms of the molecule, the pattern is formed by strong intracolumn interactions with moderately coupled columns, or by strongly linked rows that then arrange in a parallel fashion. Similar to the theoretical model, the experimental system displays a tiretrack and a wave pattern where molecules arrange in rows or columns, respectively, see Fig. [2].

experimentally the coupling in the rows and columns is significantly different resulting into two clearly distinguishable phases, although wave and tiretrack belong to the same wallpaper group. For the simulations on a coarse-grained lattice this distinction can no longer be made and both phases merge into a single tiretrack/wave pattern.

Our simulations also reproduce the sawtooth pattern, Fig. 5, which has been observed in STM measurements on Fréchet dendrons. Here three molecules form a composite which constitutes the repeat unit on a triangular lattice. In contrast the experiments report a lower wallpaper group, $p2$ rather than $p3$, since here two trimers arrange in a opposite orientation to form a unit cell, compare Fig. 2.

For the case of the jigsaw pattern, Fig. 4, we find almost perfect agreement with the STM images, both with respect to the local ordering as well as with respect to the wallpaper group.

The remaining patterns we have generated in the interaction-site model have not been found for Fréchet dendrons. The first group of patterns (Fig. 4a-c) are all highly symmetric and very similar in their respective local motifs and therefore these structures may be very sensitive to the conformation and the details of the molecule. Thus it appears promising to modify the chemical structure of the Fréchet dendron only slightly to realize also the inverted honeycomb and the honeycomb structure. The second group of simulated patterns without corresponding experimental result consists of large complex unit cell with low symmetry (Fig. 5k-i). Therefore even if some of these patterns constitute the ground state of the system it is likely that they are not realized experimentally due to kinetic barriers.

The energies of the various patterns are rather similar in agreement with the experimental observation of coexisting metastable phases. After annealing in the experiments or sufficiently many Monte Carlo steps in the simulation the patterns are expected to transform to the stable pattern. For temperatures relevant in the experiment these patterns are almost always identified with the ground state of the system. Which of the suggested patterns actually represents the ground state depends critically on the density. We exemplify the subtle interplay of the effects of packing and ordering for conformation $\gamma$ in Fig. 6 which displays one of the most complex behaviors. For high packing fractions (small lattice constant) first the honeycomb pattern and then the sawtooth pattern corresponds to the ground state. For moderate densities the tiretrack/wave exhibits the lowest energy and experimentally it also is found as the most stable pattern.

We have shown that interaction-site models are a powerful approach to model pattern formation of complex supramolecules on a substrate. In particular, the pattern diversity is correctly transferred from the molecular mechanics minimizations and also details of the patterns such as symmetries and local ordering motifs are surprisingly well reproduced. Let us discuss limitations and possible improvements of the current model. First, the interaction-site model so far accounts only for the dominant van der Waals interactions, yet on closer inspection electrostatic interactions could be also important for the selection of a particular motif. From the molecular mechanics calculations one infers that these forces are responsible for up to $30\%$ of the intermolecular interaction. It would be desirable to model also these electrostatic interactions and test if more accurate results can be achieved. Similarly, in the case of highly directional forces, such as hydrogen bonds, one should explicitly incorporate these specific interactions in the interaction-site model. Second, the model does not account for the effects of the solvent. Nevertheless some solvents interact via hydrogen bonds with the Fréchet dendrons and may favor conformations of the Fréchet dendrons where oxygen atoms are exposed to the solvent. Since the conformations are crucial for the corresponding patterns one should also account for the solvent effect in the interaction-site model. For example, one could attribute an additional conformational energy for each molecule and then compare the total energy, consisting of both conformational as well configurational energy, and thus determine the stable pattern and stable conformation in a specific solvent. Furthermore the lattices considered so far are fully occupied, which excludes complex motifs with host structures. In the interaction-site model one could account for this possibility by either a fixed partial coverage density (canonical ensemble) or a fixed chemical potential (grand canonical ensemble) and include hopping processes in addition to the rotational Monte Carlo moves. Last, we have reduced the molecule-substrate interaction to the lattice symmetry and spacing. The major justification for this simplification is that the supramolecules are significantly larger than a unit cell of the substrate and correspondingly experience only an aver-
aged adsorption energy with preferential directions. Yet, for smaller molecules, larger substrate lattice constants, or specific interactions one should include explicit space-resolved molecule-substrate interactions.

IV. CONCLUSIONS AND OUTLOOK

In this work, we have developed an interaction-site model which correctly predicts the ordered motifs of assembled monolayers. By reducing the degrees of freedom and considering the building-blocks as rigid bodies with a reduced set of interacting points, we have demonstrated that the self-organization relies on very general features of the system considered: the coupling with the substrate, the geometry of the building blocks, and their weak interactions. These are universal principles in self-organizing systems which do not depend on the specific nature of the building blocks and the underlying substrate—our method also works for substrates exhibiting different geometries. Therefore, the predictive power provided by our model may guide the synthesis of suitable building blocks to engineer arbitrary patterns for specific goals. The versatility offered to construct the building blocks makes our model especially suitable to explore a wide range of geometries.

In addition, we have shown that by combining simulated annealing with a subsequent slow heating of the system, one can not only predict the emergent patterns, but also their stability upon heating and the nature of the transition into a disordered phase. We have found that a broad variety of long-range ordered phases are stable for different geometries. A natural generalization would be to make the building blocks flexible and explore the interplay between intra and inter-molecular ordering. This extension implies including at least four new degrees of freedom per molecule, the orientations of the arms, which makes the Monte Carlo simulations computationally very expensive. An interesting alternative to speed up simulations would be to rely on genetic algorithms. They are suitable methods to compute the ground states of two-dimensional systems by minimizing the energy of single unit cells. The conformations and motifs resulting from this minimization can serve as input configurations for the Monte Carlo simulations to assess their stability. In this way, the interaction-site model is less dependent on the details of the external input. In addition, when employing genetic algorithms one can relax the constraint of the substrate. Instead considering the building blocks to be attached to the sites of a lattice, one can mimic the role of the substrate through arbitrary potentials. This opens a way to investigate systems whose substrates display more complex symmetries and interactions with the building-blocks.

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