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Reproducing morphologies of disorderly self-assembling planar molecules with static and dynamic simulation methods by matching density

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HIGHLIGHTS

- Monte Carlo and event-driven molecular dynamics approaches are discussed.
- Comparable and reproducible sets of configurations are key to validating methods.
- Statistical approaches should be used when analyzing simulated morphologies.
- When the density is fixed, static and dynamic configurations have the same structure.

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ABSTRACT

Monte Carlo and molecular dynamics simulations are the two main numerical approaches to modeling molecular self-assembly and ordering. Conceptually, however, each method explores different paths through the thermodynamic landscape. Molecular dynamics depends on the position and momentum terms. Monte Carlo is a static set, and thus the momentum term is replaced with an energy term that is dependent on the volume and entropy. Until now, it was unclear if a stochastic process of densifying particles would have the same internal structure as morphologies produced from classical mechanics. This paper provides a systematic (i.e., statistical) analysis of the outcomes of 4032 simulations for hard-core circular objects as a function of the number of molecules and the boundary conditions. Structural classification of the resultant ensembles (averaged pair correlation function, bond-order parameter, translational order parameter, and Voronoi diagrams) shows that stochastic and dynamic approaches do not alter the morphology of the steric molecules. We conclude that when the probability density of covering area fractions are matched, the ensembles produced from the two methods will show the same level of structural disorder and positional patterns. The resultant morphology from both models, therefore, is not a product of dynamic unrest, but that of the relaxation of entropic frustration from macromolecular crowding. Although statistically the two methods produce similar configurations, nuances arise from the static and dynamic nature of modeling. As a result, Monte Carlo is slightly better suited to modeling systems when the desired morphology is represented by a metastable state; molecular dynamics on the other hand is more suited to finding defects that can arise in morphologies. Regardless, a fixed density will result in similar morphologies from both techniques, driven by similar configurational entropy.

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1. Introduction

The control of supramolecular self-assembly and morphology, especially of donor–acceptor pairs, is a key feature of molecular electronics [1]. The optimized movement of charge in such systems is heavily influenced by molecular organization and morphology [2–5]. The assembly of molecules into the desired ordered and continuous phases, however, poses a significant challenge. Predictive modeling of the phase diagram of possible supramolecular architectures is a critical tool in developing the next generation of device structures [6–8].

The interplay between molecule–substrate and intramolecular interactions yielding various morphologies are most complex in the first monolayer on the substrate surface. As such the molecular tiling of a single layer of planar molecules is the focus of significant interest in modeling to predict supramolecular organization. Both molecular dynamics [9–11] and Monte Carlo [10,12,13] approaches have been successful in predicting molecular tiling patterns for a variety of planar molecules. When these two approaches are used to model similar interaction potentials and planar environments, the final properties and final states are often taken as equivalent. The conceptual basis for each method is, however, very different. Monte Carlo (MC) simulations describe the structure of the system by stochastically yet statically sampling the configuration space. This is done by reorganizing molecules (displacing and/or rotating) to minimize an energy function under certain acceptance criterion for a fixed number of molecules and fixed volume (canonical ensemble). Molecular dynamics (MD), on the other hand, describes the time evolution of all the molecules in a deterministic way by solving dynamical equations of motion until the system reaches equilibrium.

Although it has been normally assumed that both methods provide equivalent static properties, to the best of our knowledge, a systematic analysis for statistically comparing these methods has yet to be explored. A comparison between MC and MD simulations cannot be based solely on fixing the same simulation conditions across methods. The Hamiltonian of each method is substantially different. Molecular dynamics depends on the position and momentum terms. Monte Carlo is a static set, and thus the momentum term is replaced with an energy term that is dependent on the volume and entropy. Due to their unique implementations of the initial parameters (e.g. the densification rate, molecule shape and number, or interaction), building sets of reproducible results from MC and MD is an involved process resting on the understanding of how the parameters can influence the production of states. Instead of the initial state being fixed, we explored systems where in which the final outcomes are the same. If the structural characteristics of these configurations are the same, then the morphology is not a product of dynamic unrest, but that of the relaxation of entropic frustration from macromolecular crowding.

The supramolecular patterns that arise from the self-assembly of molecules are the consequence of a wide variety of interactions which are possible in semiconducting organic molecular assemblies. In any simulation approach, there are many possible interaction potentials that can be chosen to model molecular behavior [14]. The inclusion of each additional potential will fundamentally change the morphology that is produced by the simulation, and increase the complexity of comparison across approaches [15].

The simplest implementation for a potential that represents the cooperativity of planar molecules on substrates is the steric interaction. In the same way the Ising model of a two-state ferromagnet is the simplest one used to describe phase transitions [16–19], this potential is the simplest that describes the self-organization of planar molecules, based on the basic principle of the lattice gas. The microstates of the lattice gas are occupied lattice points that are restricted to only having one particle. These occupied sites are excluded from the total available volume for which any particle can move into. The entropy can then be calculated from the multiplicity of all occupied lattice points. Sometimes denoted as the excluded volume interaction or hard-core potential, this steric interaction therefore excludes all complex interactions, leaving only the entropic description of the system to determine the energy. Entropically driven self-assembly refers to the rearrangement of molecules resulting from the relaxation of entropic frustration imposed by reducing the available free volume [20,21].

Entropy has been seen to drive phase behavior as rich and complex as that seen in enthalpy driven systems [22]. Though entropy driven control of morphology is not a new concept [23], pathways to exploiting entropic control for large aromatic π-systems [24] or fullerenes [25,26] are an emerging direction in morphology control. Fullerene miscibility, a key issue for bulk heterojunctions, is often described by such excluded volume potentials [27,28,26]. For planar systems, the subtle interplay between entropy and energy driven by the steric interactions have been exploited to produce switchable supramolecular structures of naphthalenediimides [21] and arylene ethylene macromolecules [29]. Steric interactions also played a key role in the amplification of a chiral morphology in trioctyl-functionalized triazatriangulenium molecules [30]. Though limiting the complexity in the description of the intermolecular potential focuses the comparison to the simulation methods representing the morphology, these entropically driven systems are also of technological interest in morphology control.

As structural order is the main property of interest when comparing configurations, a further necessary simplification is to focus on monodispersed circular shapes for the molecules. By simplifying the shape of the molecule to a circle, it is possible to gauge the resulting localized structures against the most ordered state of disks. These patterns are generally well characterized and freely available for comparison across a variety of system sizes [31]. One system of particular interest for organic electronics that can be described by such circular excluded volume approximations are buckminsterfullerenes (C_{60}) [32]. Other non-covalently bonded macromolecules, such as micelles or colloids [33], are also well described by such approximations. Particularly in a monolayer, these systems resemble mono-dispersed circular disks, with weak steric interactions.