Enhanced Computational Sampling of Perylene and Perylothiophene Packing with Rigid-Body Models

Evan D. Miller, Matthew L. Jones, and Eric Jankowski*

Micron School of Materials Science and Engineering, Boise State University, 1910 University Dr., Boise, Idaho 83725, United States

Supporting Information

ABSTRACT: Molecular simulations have the potential to advance the understanding of how the structure of organic materials can be engineered through the choice of chemical components but are limited by computational costs. The computational costs can be significantly lowered through the use of modeling approximations that capture the relevant features of a system, while lowering algorithmic complexity or by decreasing the degrees of freedom that must be integrated. Such methods include coarse-graining techniques, approximating long-range electrostatics with short-range potentials, and the use of rigid bodies to replace flexible bonded constraints between atoms. To understand whether and to what degree these techniques can be leveraged to enhance the understanding of planar organic molecules, we investigate the morphologies predicted by molecular dynamic simulations using simplified molecular models of perylene and perylothiophene. Approximately, 10 000 wall-clock hours of graphics processing unit-accelerated simulations are performed using both rigid and flexible models to test their efficiency and predictive capability with the two chemistries. We characterize the 1191 resulting morphologies using simulated X-ray diffraction and cluster analysis to distinguish structural transitions, summarized by four phase diagrams. We find that the morphologies generated by the rigid model of perylene and perylothiophene match with those generated by the flexible model. We find that ordered, hexagonally packed columnar phases are thermodynamically favored over a wide range of densities and temperatures for both molecules, in qualitative agreement with experiments. Furthermore, we find the rigid model to be more computationally efficient for both molecules, providing more samples per second and shorter times to equilibrium. Owing to the structural accuracy and improved computational efficiency of modeling polyaromatic groups as rigid bodies, we recommend this modeling choice for enhancing the sampling in polyaromatic molecular simulations.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are an important class of materials, not least because they can self-assemble into structures that exhibit a long-range order. This spontaneous ordering can be beneficial, as in the case of organic electronic devices (particularly plastic solar cells), where ordering maximizes the intermolecular charge transport between molecules, resulting in high carrier mobilities and device efficiencies. Spontaneous aggregation of PAHs is detrimental to oil-extraction operations, where the self-assembly of asphaltene molecules leads to the rapid precipitation of tarlike aggregates that foul heat exchangers and limit crude oil processing. To control PAH aggregation, whether for new organic electronic device design or to prevent fouling in oil extraction, we require a fundamental understanding of PAH self-assembly physics.

Elucidating links between PAH chemistry and self-assembled morphologies has been limited by the difficulties associated with measuring PAH structures. Neutron scattering investigations of PAHs in solution give insights into ensemble-averaged structural features but come at the cost of requiring deuterated solvents or samples and a neutron source. In the solid state, X-ray diffraction (XRD) permits periodic features to be probed, but residual solvents and amorphous samples can complicate the analysis. Furthermore, constraints of lab space, time, and raw material cost limit the number of PAH chemistries and synthetic protocols that can be enumerated.

Computational models of molecular self-assembly are not subjected to the same space, time, and material cost constraints of wet labs and therefore permit broader explorations of large parameter spaces. The self-assembly behavior of systems ranging from organic photovoltaic mixtures, tethered nanoparticles, and copolymer melts has been successfully investigated with molecular dynamics (MD) simulations. Previous computational work has elucidated fundamental entropic contributions of particle shape on self-assembly and the transition dynamics of reconfigurable colloidal clusters. The practical limitations to performing MD simulations of every system of interest are the computational
costs of relaxing a system to equilibrium and the subsequent sampling of the equilibrium ensemble of states. Consequently, it is essential that the molecular models, computational algorithms, and computational hardware used to perform MD simulations are optimized to minimize the computational cost. Minimizing the computational cost is especially relevant for high-throughput, “Big Data” screening studies wherein thousands of simulations are performed, and a 10% improvement in efficiency can save weeks of computing.

The most detailed classical MD simulations use atomistic models, wherein interaction potentials that determine forces between atoms are derived from quantum mechanical calculations or are fit to experimental data to avoid solving wave equations explicitly. Atomistic simulations have been successfully employed to investigate protein folding, fullerene solubility, asphaltene aggregation, and polymer structure for small number of molecules. By contrast, coarse-grained models of molecules permit larger length and timescales to be accessed by representing collections of atoms as simulation elements. These coarse-grained simulations have been used to investigate morphology in organic photovoltaics, lipid bilayers, and protein structures. Even larger length scales can be accessed using phase-field methods.

With increased coarse graining comes access to longer simulation times and larger systems, at the cost of resolution that has been abstracted away. For example, one commonly used coarse-graining scheme is the united-atom model, where an explicit consideration of hydrogen is omitted. Instead, the interactions between heavier atoms are modulated to include the hydrogen interactions implicitly. This is justified, as the hydrogen atoms themselves are expected to have a negligible effect on the electronic and physical structure of a system but add significant computational costs when calculating neighbor interaction forces due to the presence of the large quantity of hydrogen in typical organic systems. United-atom models have been used in simulations to accurately predict the behavior of various systems, including polymers, proteins, and other hydrocarbons, demonstrating no significant structural differences between the united-atom and all-atom simulations or experimental data. In particular, united-atom investigations have shown good agreement with the structural and thermodynamic properties predicted through experiments for a variety of PAHs.

Another approximation technique arises from assuming that the intramolecular positional fluctuations of atoms within certain small molecules or functional groups do not significantly affect the long-range self-assembly characteristics. As such, these groups of atoms can be assumed to belong to a rigid body, where atoms are fixed in space with respect to their bonded neighbors. This can dramatically reduce the computational overhead of determining all of the bond, angle, and dihedral constraints within the system, permitting significantly longer length and timescales to be accessed. Rigid bodies are frequently implemented in systems that investigate the morphology of nanoparticle systems, using amphiphilic block copolymers or DNA to guide their self-assembly, and are shown to accurately describe the experimentally observed structures. Studies on more general “metaparticles” have shown that various structural features that are relevant to organic materials can be generated using rigid-body simulations. Rigid models have also been used to simulate aromatic hydrocarbons, showing excellent agreement with experiments for a wide range of structural properties and particle dynamics. Despite the potential for rigid models to lower the computational cost of simulating planar PAHs, systematic comparisons are lacking between flexible and rigid models used across broad sets of state points and molecular chemistries.

To describe the advances of the present work in a clearer context, we briefly summarize other, recent computational studies focusing on polyaromatic molecules. Asphaltenes have polyaromatic cores similar to the molecules studied here and require lengthy simulations of aggregate structures at many thermodynamic state points to understand their assembly physics. It is common to see simulations using the LINCS algorithm to rigidly constrain bond lengths to help access longer simulation times, but there are no examples of the rigid bodies described above to simplify the simulations of polyaromatic cores. The longest simulations, with trajectories of ~2000 ns, observe the assembly of a dozen asphaltene in water and methane under four different conditions. Atomistic simulations of 400 asphaltene molecules in vacuum access only 6 ns of simulation time. Indeed, simulations that include atomistic representations or explicit solvents generally access fewer than 150 ns for fewer than 30 molecules. Wang and Ferguson used coarse-grained models and GPU acceleration to access 500 ns trajectories for 200 asphaltenes at 27 state points, demonstrating the sampling advantages of simplified models and hardware accelerators. The work presented here extends the ideas of Wang and Ferguson, demonstrating that rigid-body models, combined with GPU accelerators, can be used to efficiently sample thousands of thermodynamic state points, by equilibrating systems of 200 molecules for over 100 ns each. A prior molecular simulation study on perylene has investigated preassembled crystal structures, whereas here we observe for the first time the spontaneous self-assembly of structures large enough, and with sufficient order, to be directly compared against the experimental grazing-incidence X-ray scattering (GIXS) data.

To study the self-assembly of rigid organic molecules using high-throughput simulation techniques, we require an understanding of which models and methods are necessary and sufficient for predicting the experimentally observed structures. Therefore, in this work, we perform united-atom MD simulations to characterize rigid and flexible models of two types of small molecules.

In this work, the PAHs perylene and perylene[1,12-bcd]-thiophene (perylothiophene) are considered as test cases, both owing to their applicability to organic electronics and similarity to the cores of complex asphaltene molecules. We consider a “flexible” model, in which the topological connectivities and geometries are enforced by bond, angle, and dihedral constraints, and compare the computational performance and the resultant packing morphologies with the rigid model, when these constraints are fixed. The rigid model considerably improves computational efficiency by permitting a larger quantity of time steps to be accessed per second, without significantly increasing the relaxation or autocorrelation timescales or affecting the obtained morphologies. In the Methods section, we describe the simulation methodology, along with details on the molecular topologies and the analysis metrics we use. In the Results section, we discuss the thermodynamically stable morphologies predicted with the two molecules and two models, demonstrating that experimentally observed phase transitions are reproduced. Finally, we conclude by considering the quantitative implications of modeling organic molecules as...
rigid bodies, comparing our predictions with experimental measurements, and highlighting opportunities for future work.

**METHODS**

MD simulations are performed to determine the thermodynamically stable morphologies of perylene and perylothiophene as a function of temperature and packing fraction for both rigid and flexible models. Equilibration and sampling metrics are computed from time series of potential energy and structural metrics. The structural metrics are computed from the resulting morphologies to distinguish "vapor", "droplet", "ordered", and "eclipsed" morphologies, which are summarized in phase diagrams.

**MD Simulations.** MD simulations are performed using the HOOMD-blue simulation suite to predict the thermodynamically stable morphologies for perylene and perylothiophene (Figure 1a,b, respectively). These are performed in the canonical ensemble (constant number of molecules $N$, volume $V$, and temperature $T$), using a Nosé–Hoover thermostat to control the temperature. Particle positions and velocities are updated with two-step velocity-Verlet integration of Newton’s equations of motion with a time step of $dt = 0.001$ dimensionless time units. We run periodically bound simulations of systems containing 200–1500 molecules until the equilibrium is reached based on the stabilization and autocorrelation of observables, including potential energy and structural symmetries and to compare simulated GIXS patterns with experimentally observed ones. Section S4 summarizes the range of temperatures and densities studied in this work along with temperature and density steps.

**Structural Analysis.** Molecular packing is quantified by four metrics: the center-of-mass radial distribution function $g(r)$, orientational correlations among neighboring molecules $\xi$, a degree-of-crystallinity metric $\psi$, and with simulated GIXS characterization. The metrics $g(r)$, $\xi$, and $\psi$ are used in concert to distinguish the vapor, droplet, ordered, and eclipsed phases. Simulated GIXS patterns are used to identify periodic length scales and structural symmetries and to compare simulated morphologies against experimentally synthesized materials. These GIXS patterns are computed using numerical Fourier techniques, as described in refs 13 and 66. Calculating $g(r)$ between molecular centers of mass provides data to justify molecular-clustering criteria. Two key length scales are determined from $g(r)$ of ordered morphologies, $R_{cut}$ and $R_{out,cut}$, which are used to distinguish the molecules that are nearest neighbors in a “stack” and the molecules that are in neighboring stacks, respectively. The in-stack cutoff distance $R_{cut} = 5.0$ Å is chosen as a clustering criterion based on the location of the first minimum in $g(r)$, following the nearest-neighbor peak at $r = 3.5$ Å (Figure 2a). The neighboring-stack cutoff distance $R_{out,cut} = 11.6$ Å is determined by the geometric average

$$R_{out,cut} = \sqrt{\frac{R_{cut}^2}{2}} \quad (1)$$

Figure 1. Molecular structures of (a) perylene and (b) perylothiophene. United-atom topologies for (c) perylene and (d) perylothiophene. Blue spheres represent C atoms (inner ring) or C–H beads (outer rings), yellow spheres represent S atoms, and blue/yellow cylinders represent bonds of the respective bead type. Arrows are drawn to indicate the vectors that are used to describe the orientation of the molecules, both in-plane and normal to the plane of the molecules.
of the nearest-neighbor peak ($r = 5.0 \text{ Å}$) and the stack-center to stack-center distance ($r = 10.5 \text{ Å}$) determined from the third-nearest-neighbor peak of $g(r)$ (Figure 2a).

The orientational order parameter $\xi$ is calculated for a simulation snapshot by averaging the local orientational order

$$O_{ij} = \vec{a}_i \cdot \vec{a}_j$$

over all pairs of neighboring molecules, where $a_i$ and $a_j$ are the unit orientation vectors for molecules $i$ and $j$ whose COM separation is less than $R_{\text{cut}}$.

The in-plane orientation vector $a$ for perylene is defined to be orthogonal to the bonds connecting naphthalene rings and is depicted by a black arrow in Figure 1c. In peryloiphene, the direction of orientation vector $a$ is defined from the center-of-mass of the perylene core to the sulfur atom, as shown in Figure 1d. A system is considered eclipsed when $\xi \geq 0.9$. This cutoff is chosen based on the evolution of $\xi$ as a function of $T$ at the densities studied here, which shows that 0.9 is a sensitive cutoff distinguishing molecular stacks that are in and out of register (section S5).

The crystallinity order parameter $\psi$ is calculated for a simulation snapshot as the fraction of molecules in large “clusters”. Here, two molecules $i$ and $j$ are considered to be part of the same cluster when $r_{ij} \leq R_{\text{cut}}$ and when $\theta_{ij} < \theta_{\text{cut}}$. The alignment of two molecules $\theta_{ij}$ is calculated from the dot product of their out-of-plane unit vectors (Figure 1c,d). $\theta_{\text{cut}}$ is determined from the distribution of the dot products between the normal vectors of molecules (section S6). Clusters comprising 30% or more of the system (60+ molecules) are considered “large”. This metric is chosen to distinguish ordered morphologies containing a few large clusters, whereas droplet and vapor configurations contain many small clusters. Figure 2b shows a configuration with three clusters (colored blue, green, and red), identified using this clustering protocol. The “large cluster” cutoff of 30% is chosen to balance overcounting of small clusters against undercounting large clusters, based on visual inspection using Visual Molecular Dynamics.

The gaseous vapor phase distinguished here is characterized by low molecular association (no defined peaks in $g(r)$), low orientational correlations $\xi \leq 0.9$, and low crystallinity $\psi \leq 0.5$ as expected at low densities and high temperatures. The liquid droplet phase is distinguished by significant aggregation (first peak is the only defined peak in $g(r)$), with low orientational correlations $\xi \leq 0.9$ and low crystallinity $\psi \leq 0.5$. At high temperatures and pressures, these liquid and gaseous phases become indistinguishable and so are characterized instead as a “fluid” phase. The solid ordered phase is distinguished by well-defined first-, second-, and third-nearest-neighbor peaks in $g(r)$ (Figure 2a), low orientational correlations $\xi \leq 0.9$, and high crystallinity $\psi \leq 0.5$. In this work, ordered phases are characterized by hexagonally packed columns of molecules (Figure 3), demonstrating significant $\pi$-stacking (Figure 2b).

The eclipsed phase shares the $g(r)$ peak structure of the ordered phase but has high orientational correlations $\xi \geq 0.9$ and high crystallinity $\psi \geq 0.5$. As in the ordered phase, $\pi$-stacking is prevalent in the eclipsed phase but differs in that molecules in a stack share the same orientation.

At low densities ($<0.65 \text{ g/cm}^3$), we consider an additional criterion to distinguish vapor and droplet phases. Here, average $g(r)$ values in the range of $9.3 \leq r < 10.9 \text{ Å}$ (gray highlight in Figure 1a) are compared with those present in the highest temperature, most dispersed system. This range is chosen to allow long-range order comparisons between simulations,
without taking into account the short-range π-stacking present in all samples. If the average $g(9.3 \leq r < 10.9)$ for the lower temperature sample is within 10% of that for the highest temperature, most dispersed trial, then the system is considered to be a vapor. An example of this characterization methodology is shown in Figure 2a. Here, for $9.3 \leq r < 10.9$ Å, the 1163 K system (black dashed line) is within 10% of the 1837 K system (green line), representing the vapor system, and so, the 1163 K system is also considered to be a vapor. At lower temperatures, the 918 K system (blue line) is shown to be more than 10% of $g(r)$ of the vapor, and so, this morphology more closely represents a droplet. As the temperature decreases further (red line, 612 K), the morphology is significantly more ordered than the vapor phase, and the $g(r)$ peaks become even more defined. Thus, $g(r)$ is used to determine the phase transition temperatures from strongly ordered to droplet to vapor.

Using these criteria to distinguish the structures resulting from our MD simulations, we summarize how the assembled morphologies of perylene and perylothiophene depend on temperature, density, and model flexibility in four phase diagrams (Figure 4). Each phase diagram is divided into five regions: vapor (green), fluid (cyan), droplet (blue), ordered (red), and eclipsed (magenta). At high temperatures ($T > 1700$ K), vapor phases are observed at low densities and fluid phases at high densities. All four phase diagrams show a phase boundary between fluid phases and ordered phases at higher densities ($\rho > 0.65$ g/cm$^3$), although the disordered–ordered transition temperatures $T_{DO}$ vary. Another common feature is the phase boundary between the ordered and eclipsed phases at lower temperatures across the full range of densities studied. Finally, all four phase diagrams indicate regions of phase space with droplets located between the ordered and vapor phases at low densities ($\rho < 0.65$ g/cm$^3$). At densities greater than 0.65 g/cm$^3$, the droplet and vapor phases are indistinguishable.

We find that the phase diagrams for rigid models of perylene and perylothiophene are similar to their flexible counterparts. For perylene, the phase boundaries between the droplet phase and the vapor, fluid, and ordered phases are nearly identical with both models. The phase boundary between fluid and ordered phases is also similar between rigid and flexible perylene, although we observe significantly higher $T_{DO}$ for the

**RESULTS**

Initial simulation results demonstrate no differences in structural metrics $\psi$, $\xi$, and $g(r)$ for systems of 200–1500 molecules (section S7). Owing to the significantly faster relaxation times and simulation times, we therefore focus on systems of 200 molecules and report the results in this section. Systems of 200 molecules require on average 20 ns of simulation time to reach equilibrium, followed by on average 115 ns of sampling time. Potential energy and $\psi$ autocorrelation times are calculated to ensure at least 20 uncorrelated snapshots are generated during the sampling period. If fewer than 20 independent snapshots are generated, simulations are run longer until this criterion is satisfied.

**Phase Diagrams.** Using $g(r)$, $\xi$, and $\psi$ to differentiate morphologies resulting from our MD simulations, we summarize how the assembled morphologies of perylene and perylothiophene depend on temperature, density, and model flexibility in four phase diagrams (Figure 4). Each phase diagram is divided into five regions: vapor (green), fluid (cyan), droplet (blue), ordered (red), and eclipsed (magenta). At high temperatures ($T > 1700$ K), vapor phases are observed at low densities and fluid phases at high densities. All four phase diagrams show a phase boundary between fluid phases and ordered phases at higher densities ($\rho > 0.65$ g/cm$^3$), although the disordered–ordered transition temperatures $T_{DO}$ vary. Another common feature is the phase boundary between the ordered and eclipsed phases at lower temperatures across the full range of densities studied. Finally, all four phase diagrams indicate regions of phase space with droplets located between the ordered and vapor phases at low densities ($\rho < 0.65$ g/cm$^3$). At densities greater than 0.65 g/cm$^3$, the droplet and vapor phases are indistinguishable.

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rigid model at high densities ($\rho > 1.5\ g/cm^3$). The transition temperatures between ordered perylene and eclipsed perylene also slightly shift higher for the rigid model relative to the flexible model (and more so at $\rho = 1.77\ g/cm^3$) but generally are within 90 K of each other. For perylophophene, the rigid and flexible phase diagrams are nearly identical. As with perylene, there is a shift in $T_D$ observed at high densities. At low densities, we observe discrepancies between the rigid and flexible phase boundaries between the droplet, vapor, and ordered phases.

The phase diagrams for perylene and perylophophene are qualitatively similar in that they each contain the same five phases arranged similarly. One difference is that the phase boundaries between ordered and fluid/vapor phases of perylophophene occur at higher temperatures than those observed for perylene. Additionally, the phase boundary between the ordered and eclipsed phases for perylophophene is at lower temperatures than that observed for perylene. This demonstrates that the addition of a single heteroatom (the difference between perylophophene and perylene) is enough to significantly broaden the thermodynamic stability of an ordered morphology (here, hexagonally packed cylinders) over a wide region of state space.

Overall, we find that the rigid models of perylene and perylophophene give comparable structural results to their flexible counterparts. The discrepancy between rigid and flexible models at high densities is not surprising. At high densities, flexible molecules can compress to relieve stresses imposed by the crowded molecules nearby, whereas rigid molecules cannot. This observation is consistent with entropic considerations (which depend sensitively on degree-of-freedom constraints), determining the phase behavior of densely packed shapes.6,70 The densities at which the rigid model differs substantially from the flexible model are significantly higher than experimentally observed densities for these molecules. We therefore conclude that rigid models of perylene and perylophophene give comparable structural results to their flexible model counterparts and are appropriate for mapping out the phase space.

This is further justified by the correspondence between our simulated perylene transition temperatures and those from experiments. In an investigation by Botoshansky, Herbstein, and Kapon, the phase boundary between melted perylene and crystalline $\alpha$-perylene was found at $\approx 600\ K$, and the phase boundary between $\alpha$-perylene and $\beta$-perylene was found at $\approx 450\ K$.71 These temperatures agree well with the $\approx 600$ and $\approx 400\ K$ phase boundaries between fluid/ordered and ordered/eclipsed phases observed in this work at experimental densities (1.28 $g/cm^3$).

Molecular Packings. In the ordered phase, rigid and flexible models of perylene and perlyophophene self-assemble hexagonally packed columns (Figure 3a,b), at temperatures near 600 K. The center-of-mass radial distribution function $g(r)$ shows nearly identical structural correlations among these four models, with flexible perylene demonstrating slightly different ordering length scales (Figure 5). For these ordered structures, shown in Figure 3a,b, the first $g(r)$ peak corresponds to π-stacking and is located at 3.50 Å in flexible perylene. We measure π-stacking distance for both models of pelylophophene and the rigid model of perylene to be 3.44 Å. We therefore conclude that the rigid model faithfully reproduces the major packing features of its flexible counterpart for perylene and perylophophene, with no $g(r)$ peak varying more than 0.1 Å between the two models.

Perylene Morphologies. At temperatures below the disordered–order transition temperature $T_D$, we observe perylene systems with $\rho > 0.85\ g/cm^3$ self-assembling into ordered morphologies. We observe a second phase transition between ordered and eclipsed morphologies at even lower temperatures. The ordered morphologies are characterized by stacks of perylene molecules arranged hexagonally, as shown in Figure 3. The stacks of molecules in ordered morphologies have no orientational correlations along the stacking axis. In eclipsed morphologies, all of the perylenes in a stack have identical orientations, as shown in Figure 6. Furthermore, we observe that the orientationally ordered stacks in eclipsed morphologies can aggregate in both checkerboard (Figure 6a) and aligned (Figure 6b) motifs. In the checkerboard case, adjacent stacks have orientation offset by 90°. In the aligned case, adjacent stacks have identical orientations. The potential energy of the checkerboard motif ($-275.13 \pm 0.17e$) is slightly lower, but very close to that of the aligned motif ($-275.95 \pm 0.17e$) (section S8).

Simulated GIXS patterns of ordered and eclipsed morphologies (Figure 7a) are qualitatively similar to experimental GIXS patterns of $\beta$-perylene crystals (Figure 7b, adapted with permission from Ishii and Miyasaka).72 We observe in-plane reflections (labeled 110 in Figure 7b) which correspond to π-stacking and out-of-plane reflections (labeled 001 in Figure 7b), corresponding to columnar packings. We do not observe (111) and (120) peaks, corresponding to the glide planes that describe the symmetry between columns in our simulated GIXS patterns. We find, using both GIXS and $g(r)$ analyses, a π-stacking distance of 3.4 Å, which is in good agreement with 3.47 Å found in $\alpha$-perylene.73,74

The local structures of the ordered and eclipsed perylene morphologies observed here differ from the experimentally observed $\alpha$ and $\beta$ polymorphs of perylene.73–75 The herringbone arrangements observed in $\alpha$ and $\beta$ perylene are not observed in our simulations and are the primary structural difference. Lattice parameters for $\beta$-perylene have been measured experimentally as: $a = 9.76$, $b = 5.84$, and $c = 10.61\ \AA$.76,77 We calculate the lattice parameters for aligned, eclipsed morphologies to be: $a = 7.36$, $b = 3.33$, and $c = 9.12\ \AA$. The parameter $b$ is significantly smaller in the simulated
morphologies, as the perylene stacks are orthogonal to the \( b \) axis in this investigation, instead of the flattened-out herringbone/\( \gamma \)-structure often observed experimentally in the \( \beta \) phase.\(^7\) For the checkerboard, eclipsed morphologies, we calculate lattice parameters: \( a = 11.46 \), \( b = 3.33 \), and \( c = 16.22 \) Å, which are further from \( \beta \)-perylene parameters than the aligned, eclipsed morphologies. Scattering patterns for the two structures are also shown in Figure 6e,f with the corresponding morphologies in (c) and (d). The scattering patterns shown in Figure 6e,f are similar to that of the \( \beta \)-perylene structure shown in Figure 7b, wherein we observe reflections owing to \( \pi \)-stacking and columnar formations.

It is not surprising that the rigid and flexible models of perylene studied here do not perfectly capture the crystalline structures of experimentally characterized perylene polymorphs. Our modeling choice to neglect long-range electrostatics is expected to influence the thermodynamic stability of molecular packings.\(^6\) Furthermore, the Lennard-Jones interaction parameters and bond lengths chosen in this work are “off-the-shelf” OPLS parameters that have not been optimized for perylene. With these modeling assumptions in mind, we conclude that our simple models of perylene satisfactorily predict the broad phase behavior and reproduce many of the structural features of perylene polymorphs observed in experiments.

**Perylothiophene Morphologies.** As with perylene, below \( T_{\text{DP}} \), systems with \( \rho \geq 0.91 \) g/cm\(^3\) self-assemble into ordered morphologies that are characterized by hexagonally arranged columns of \( \pi \)-stacked perylothiophene molecules (Figure 3b). We observe another similarity between perylene and perylothiophene in the \( \pi \)-stacked columns shown in Figure 8a, which is quantified in the simulated GIXS pattern (Figure 8c). Hexagonally packed features (Figure 8b) are also present,

**Figure 6.** (a) Checkerboard and (b) aligned structural motifs found in low-temperature runs for both rigid and flexible perylene. These are colored red and blue to highlight the different orientations. In the aligned simulation, there exists a small, differently oriented crystal that is colored gray. Structures for low temperature (c) checkerboard and (d) aligned systems of perylene, with the corresponding simulated GIXS patterns for (e) checkerboard and (f) aligned systems.

**Figure 7.** (a) Simulated scattering results for hexagonally packed columns and (b) experimental XRD pattern for \( \beta \)-perylene, reproduced with permission from Ayumi Ishii and Tsutomu Miyasaka.\(^7\) Copyright 2012 Royal Society of Chemistry.

**Figure 8.** Perylothiophene structural features. (a) Side-view simulation snapshot showing \( \pi \)-stacked columns. (b) Top-view snapshot showing hexagonally packed columns. (c) Simulated GIXS pattern taken from the side and (d) from the top. (e) A single, orientationally uncorrelated stack of perylothiophene at 550 K and (f) an orientationally correlated stack at 360 K. (g) Top-view simulation snapshot at 360 K in which columns of perylothiophene form staggered conformations.
as can be seen in the corresponding simulated GIXS pattern (Figure 8d). The stacks of perylothiophene molecules have no orientational bias within the ordered stacks at higher temperatures, T > 400 K. However, as temperature decreases (below ~400 K), sulfur atoms aggregate along the perylothiophene stacks to form an eclipsed phase in which perylothiophene molecules within the stack have the same in-plane orientation (Figure 8e,f). Beyond increased aggregation and order within columns, we additionally find that the perylothiophene columns within the eclipsed phase arrange in a staggered formation, with increased anisotropy between them, as shown in Figure 8g.

Unlike perylene, perylothiophene tends not to assemble into an α-herringbone structure and so exists only as a single, flattened-herringbone β polymorph. This difference is likely due to the more strongly ordered π-stacking arising from the balance between the dispersion force and electrostatic interactions between the sulfur atoms in the thiophene ring.62 The local structure of the ordered and eclipsed phases is similar to that of the crystal structure determined by Santos and co-workers containing regular π-stacking of perylothiophene molecules within the system.65 Within the ordered phase, we measure an interplanar distance of 3.44 Å and an intercolumnar distance of 10.50 Å. However, the eclipsed phase resembles the experimentally determined structure more closely, owing to the presence of aligned perylothiophene molecules that are in a staggered conformation. We measure lattice parameters a = 9.34 Å, b = 3.49 Å, and c = 8.42 Å in the eclipsed state. These results broadly agree with those reported from experiments by Santos and co-workers: a = 8.46 Å and c = 8.95 Å, whereas the b parameter is in excellent agreement b = 3.52 Å.65 The intercolumnar distances, along with the a and c lattice parameters, are different because our model predicts that the perylothiophene molecules stack perpendicularly to the b axis and not at an angle of 39.84°, as observed in experiments. Despite these structural differences, the similarity in our results and experimental structures indicates that our model successfully describes much of the key physics governing self-assembly in perylothiophene.

Performance. The absolute performance of a computational model depends on three factors: the number of TPS that can be calculated, the number of time steps required for the random initial configuration to relax to equilibrium (τr), and the number of time steps between statistically independent frames (τs) determined from autocorrelations in the potential energy and structural metric time series. It is useful to consider these parameters in terms of the “wall-clock time”, normalizing τr and τs by TPS to determine τr and τs. To evaluate the computational performance of rigid and flexible models, we compare τr and τs between the models in disordered, ordered, and eclipsed regimes. Performance is summarized in Table 1, where the nonbonded contributions to potential energy Uij and the crystallinity order parameter ψ each are used to calculate relaxation and autocorrelation times. Values of τr and τs are normalized by the flexible model Uij-determined values to give absolute relative performance values. For instance, the calculated value of τr = 0.17 for rigid disordered perylene indicates that the rigid model relaxes to equilibrium 5.88 times faster than the flexible model, if ψ is used as a structural metric instead of Uij. Conversely, the calculated value of τs = 3.51 for rigid, ordered perylene indicates that independent samples are generated 3.51 times more slowly than the flexible model, if ψ is used as a structural metric instead of Uij. For each flexible—rigid pair of data in the system, the lower number of the two indicates the more efficient simulation methodology as relaxation or a statistically independent frame has been obtained more quickly. These data are included un-normalized and in full in section S9.

Sampling times τs are generally larger when determined by autocorrelations in the degree of crystallinity ψ than when determined by Uij autocorrelations. This observation is important because potential energy is frequently used as a proxy for the molecular structure, and we show here that a direct measure of structures decorrelates more slowly than potential energy. We therefore use autocorrelation times calculated from ψ as the more conservative and accurate metric for both structural sampling and performance comparisons.

For the state points studied here, initial relaxation to equilibrium is a small fraction of the total simulation time compared with sampling the equilibrium distribution. We find that the time required to relax to equilibrium as measured by ψ is faster than that measured by Uij. Furthermore, we find that the rigid model is generally more efficient than the rigid model at relaxing to equilibrium, independent of whether the simulations are performed at disordered, ordered, or eclipsed regions of the phase space (Table 1). The only outlier to this is the case of eclipsed perylothiophene morphologies, where we find the rigid model to take 1.2 (Uij) to 1.45 (ψ) times as long as the flexible model to reach equilibrium.

|          | perylene     |         | perylothiophene |         |
|----------|--------------|---------|-----------------|---------|
|          | Uij          | ψ       | Uij             | ψ       |
| flexible |             |         | flexible        |         |
| rigid    | 1.00         | 0.28    | 0.17            |         |
| ordered  | 1.00         | 0.66    | 0.19            |         |
| eclipsed | 1.00         | 0.70    | 0.07            |         |

The time taken to relax to equilibrium τr and autocorrelation time τs are determined by normalizing τr and τs by the TPS for each case, respectively. Values of τr and τs are normalized to the performance of the flexible model for each molecule calculated using Uij. Smaller numbers indicate better performance.

The apparent flexibility of the perylothiophene backbone is in excellent agreement with the presence of aligned perylothiophene molecules that are in the experimentally determined structure more closely, owing to the distance of 10.50 Å. However, the eclipsed phase resembles the 9.34, b broad agreement with those reported from experiments by Santos and colleagues containing regular π-stacking of perylothiophene molecules within the system.65 Within the ordered phase, we measure an interplanar distance of 3.44 Å and an intercolumnar distance of 10.50 Å. However, the eclipsed phase resembles the experimentally determined structure more closely, owing to the presence of aligned perylothiophene molecules that are in a staggered conformation. We measure lattice parameters a = 9.34 Å, b = 3.49 Å, and c = 8.42 Å in the eclipsed state. These results broadly agree with those reported from experiments by Santos and co-workers: a = 8.46 Å and c = 8.95 Å, whereas the b parameter is in excellent agreement b = 3.52 Å.65 The intercolumnar distances, along with the a and c lattice parameters, are different because our model predicts that the perylothiophene molecules stack perpendicularly to the b axis and not at an angle of 39.84°, as observed in experiments. Despite these structural differences, the similarity in our results and experimental structures indicates that our model successfully describes much of the key physics governing self-assembly in perylothiophene.

**Performance.** The absolute performance of a computational model depends on three factors: the number of TPS that can be calculated, the number of time steps required for the random initial configuration to relax to equilibrium (τr), and the number of time steps between statistically independent frames (τs) determined from autocorrelations in the potential energy and structural metric time series. It is useful to consider these parameters in terms of the “wall-clock time”, normalizing τr and τs by TPS to determine τr and τs. To evaluate the computational performance of rigid and flexible models, we compare τr and τs between the models in disordered, ordered, and eclipsed regimes. Performance is summarized in Table 1, where the nonbonded contributions to potential energy Uij and the crystallinity order parameter ψ each are used to calculate relaxation and autocorrelation times. Values of τr and τs are normalized by the flexible model Uij-determined values to give absolute relative performance values. For instance, the calculated value of τr = 0.17 for rigid disordered perylene indicates that the rigid model relaxes to equilibrium 5.88 times faster than the flexible model, if ψ is used as a structural metric instead of Uij. Conversely, the calculated value of τs = 3.51 for rigid, ordered perylene indicates that independent samples are generated 3.51 times more slowly than the flexible model, if ψ is used as a structural metric instead of Uij. For each flexible—rigid pair of data in the system, the lower number of the two indicates the more efficient simulation methodology as relaxation or a statistically independent frame has been obtained more quickly. These data are included un-normalized and in full in section S9.

Sampling times τs are generally larger when determined by autocorrelations in the degree of crystallinity ψ than when determined by Uij autocorrelations. This observation is important because potential energy is frequently used as a proxy for the molecular structure, and we show here that a direct measure of structures decorrelates more slowly than potential energy. We therefore use autocorrelation times calculated from ψ as the more conservative and accurate metric for both structural sampling and performance comparisons.

For the state points studied here, initial relaxation to equilibrium is a small fraction of the total simulation time compared with sampling the equilibrium distribution. We find that the time required to relax to equilibrium as measured by ψ is faster than that measured by Uij. Furthermore, we find that the rigid model is generally more efficient than the rigid model at relaxing to equilibrium, independent of whether the simulations are performed at disordered, ordered, or eclipsed regions of the phase space (Table 1). The only outlier to this is the case of eclipsed perylothiophene morphologies, where we find the rigid model to take 1.2 (Uij) to 1.45 (ψ) times as long as the flexible model to reach equilibrium.
Comparing the autocorrelation times $t_\psi$ as measured by $\psi$ in Table 1, we find that the rigid model offers significant performance benefits when sampling independent configurations. The rigid model is 3.2 times faster sampling disordered perylene than the flexible model, 1.47 times faster sampling ordered perylene, and 1.64 times faster sampling eclipsed perylene. For perylothiophene, the rigid model is 11.5, 1.36, and 2.2 times faster sampling ordered, disordered, and eclipsed phases, respectively. The factor of 11.5 times better performance sampling disordered configurations of perylothiophene could be particularly important in the simulation of asphaltene systems that include heteroatoms and have interesting disordered aggregation behavior. Because the sampling portion of these simulations is the majority of simulation time and because the aggregation behavior. Because the sampling portion of these simulations is the majority of simulation time and because the rigid model offers a factor of 1.36–11.5 times better performance sampling statistically independent structures, we recommend using rigid bodies to model polyaromatic hydrocarbons when appropriate.

**MD CONCLUSIONS**

MD simulations are used to investigate the self-assembly of perylene and perylothiophene systems using a simplified molecular model. Perylothiophene is shown to self-assemble hexagonally packed columns over a broader region of the phase space than perylene, a consequence of the added sulfur atom. Our models reproduce the structural features of these molecules observed in experiments (where available), reproducing the $\pi$-stacking distances of $\alpha$-perylene, and simulated GIXS analysis shows morphologies with features observed in $\beta$-perylene. The predicted structures of perylothiophene match well with the lattice parameters determined experimentally, particularly at lower temperatures, where we see the emergence of staggered perylothiophene rings wherein sulfurs aggregate along the columns. While the simplified united-atom model used here captures much of the key physics governing perylene and perylothiophene self-assembly, we note differences in lattice parameters and the local molecular structure between the morphologies observed here and experiments. In particular, the herringbone arrangement of perylene molecules observed in $\alpha$ and $\beta$ polymorphs is not observed in this work. Preliminary simulations indicate that herringbone arrangements emerge when long-range electrostatics are included.

We find close agreement between the phase transitions in experimental works and the phase diagrams generated with both flexible and rigid models. The only caveat found is that at high densities, where confinement effects are most pronounced, the rigid model and flexible models differ in their thermodynamically stable packings. We show that potential energy autocorrelations underpredict how fast the structure is evolving in these systems and demonstrate that the rigid model offers 1.36–11.5 times enhanced sampling per second. We therefore propose the use of rigid models to accelerate the simulation of polyaromatic hydrocarbons. In particular, these models offer promise to investigate assemblies of asphaltenes in solution and alternative electron acceptors in photovoltaics, two fields that require access to long aggregation timescales.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00371.
