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Towards Molecular Dynamics Modelling of Mesoscale Bulk Heterojunction Morphologies

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Motivation
The performance of organic photovoltaics (OPVs) based on solution processed polymer:fullerene or polymer:polymer active layers is crucially dependent on the 3D morphology of the mesoscale bulk heterojunction. Here, we use Molecular Dynamics (MD) simulations of single indacenodithiophene-co-benzothiadiazole (IDTBT) polymers in solution to study their persistence lengths, since long persistence lengths are believed to be crucial for high charge mobilities and strong optical absorption. Furthermore, we present initial efforts towards simulating the dynamics of blend microstructure formation at reasonable computational costs by employing coarse-grained (CG) MD models, i.e. describing several atoms in a unified manner. Through this, we hope to aid the interpretation of experimental 3D imaging and refine the current, predominantly phenomenological, hypotheses which are based on indirect experimental probing of 3D morphology.

Persistence length simulations
For an oligomer consisting of \( N \) repeat units, its persistence length can be estimated by an angle correlation function quantifying the mean angle \( \Theta \) between vectors across different repeat units:

\[
C_n(\Theta) = \langle |\cos \Theta_{i,i+n}| \rangle_l \\
= \frac{1}{N-n} \sum_{i=1}^{N-n} |\mathbf{v}_i \cdot \mathbf{v}_{i+n}| \\
\]

In order to extract a quantitative measure for persistence length, \( n_p \) (in units of repeat units), we fit an exponential of type:\(^1,^2\)

\[
C_n(\Theta) \sim e^{-n/n_p} 
\]

Figure 1: Persistence length simulations of 2-ethylhexyl-IDTBT of different lengths; a 12mer (red) in all-atom (AA) chloroform and a 32mer (black) in coarse-grained (CG) chloroform. Both exponential fits are terminated at \( n = 12 \).

Figure 2: Snapshots of 2-ethylhexyl-IDTBT in chloroform; the two top ones are taken at the same time from different angles to highlight the stiff ribbon-like structure of IDTBT.

Coarse-graining the systems
Using the MARTINI force field\(^2\) to coarse-grain our systems, the time- and length-scales relevant for morphology evolution are within reach of MD simulations:

\( >400 \) times speed-up

We can thus simulate mesoscale bulk heterojunction morphologies in 3D,\(^4,^5\)

Figure 3: All-atom and MARTINI coarse-grained models for chloroform (CF), PCBM,\(^5\) and a dimer of C\(_{100}\)IDTBT; bonds and constraints between interaction sites are marked with solid rods and the bead sizes by semi-transparent spheres.

Figure 4: 30x30x10 nm slab of C\(_{100}\)IDTBT 12mers (red) and PCBM (semi-transparent grey) annealed at 600 K for 50 ns and cooled down to 300 K. Sidechains are not shown.

Future work
We are presently extending the work on persistence lengths with a broader analysis and comparison to SAXS experiments, while we aim to use coarse-grained MD models in combination with in-situ X-ray analysis of OPV active layers to gain insight into the morphology evolution during solution processed roll-to-roll printing.\(^5\)

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Methods
We have used the GROMACS 2016.3 package\(^6\) for all MD simulations. The OPLS-AA force field and Ref. 8 formed the basis for the all-atom simulations of IDTBT but with our own parametersizations of e.g. the IDT-5T torsional potential. The coarse-grained simulations were based on the MARTINI force field\(^5\) and in part Ref. 5.

References