

A Molecular Dynamics Lennard-Jones Chain model for Phase Separation Behavior of Polythiophene and Fullerene Mixtures

Isaac Riisness
June 13, 2012

Organic photovoltaic materials employ conjugated polymers and fullerene-based molecules to absorb photons and transport captured charges. The phase separation during processing in these systems is critical for their efficiency. To that end, phase separation and dynamics of polythiophene ($M= 2, 4, 10, 20, 40, 60$), fullerene mixtures are investigated using (NVE) molecular dynamics with a Lennard-Jones chain force-field. Radial distribution functions show a slight increase in fullerene packing after system has been annealed at $T=1.5$ dimensionless temperature, in agreement with experimental data. Polythiophene diffusion constants follow a power law relationship based on polymer length.

Organic photovoltaics (OPVs) [1] are an important part of solar energy research because they offer potential low cost, easy-to-process, alternatives to traditional silicon or rare-earth based solar cells. Typically, OPVs contain two active materials: a conjugated polymer semiconductor (often a poly-thiophene derivative), which splits absorbed photons into an electron/hole pair (exciton), and a fullerene-based electron-acceptor, which separates the bound electron/hole pair. After the exciton is separated, the electron is transported on the fullerene material to an electrode for energy harvest; the hole, left behind on the conjugated polymer, diffuses to the other electrode, completing the circuit (fig. 1a). Understanding the biphasic (conjugated-polymer, fullerene) charge transport network remains a key challenge in OPV research and will enable higher efficiencies (currently ~10% vs ~20% for polycrystalline silicon).

OPVs devices are prepared by spin casting polymer:fullerene mixtures from solution into films, which are thermally annealed (150C for 5-30min) to encourage slight phase separation (fig. 1b) and create the biphasic charge transport network. To better understand the process of diffusion and phase separation during OPV processing, this work presents a simple, two component Lennard-Jones (LJ) chain molecular-dynamics (MD) model where thiophene monomers polymerize via a harmonic potential, and other interactions (non-bonded thiophene-thiophene, fullerene-fullerene, thiophene-fullerene) are modeled with 6-12 LJ potentials (fig. 2). The well-depth and van der waals LJ parameters (ϵ and σ , respectively) for thiophene-thiophene [2] and fullerene-fullerene [3] interactions were taken from full atomistic density functional theory calculations (fig. 2). Harmonic bond parameters (r_0 and k) for bonded thiophene monomers were estimated using an effective conjugation coordinate model for short polythiophene oligomers [4].

To minimize simulation expense, the LJ potential for non-bonded particles was cut and shifted at a distance of $r_c = 2.5\text{nm}$. Pairwise interactions (energy, forces, etc.) and other expensive calculations (velocity-verlet integrator) were computed using Fortran 90; whereas less expensive or infrequent tasks (file reading/writing, $g(r)$, mean squared displacement) were accomplished with custom Python(x,y) code. F2PY was used interface between the Fortran and Python code. Simulations began by allowing a random lattice of thiophene and fullerene molecules ($N=240$, total) to relax to a minimum energy configuration using a conjugate gradient procedure. Next, the system was allowed to

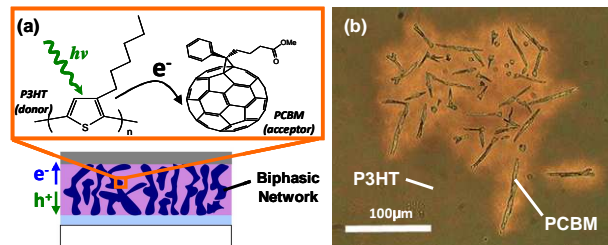


Figure 1: (a) Photon capture and charge transfer process in the popular poly-3-hexyl thiophene (P3HT): phenyl-C61-butyric acid methyl ester (PCBM) organic solar cell. (b) Bright-field image of over-annealed (160C, 30min) film displays PCBM agglomerates on P3HT with characteristic “depletion” halo.

$$U = \sum_{i < j, ij \text{ not bonded}} 4\epsilon \left[\left(\frac{r_{ij}}{\sigma} \right)^{-12} - \left(\frac{r_{ij}}{\sigma} \right)^{-6} \right] + \sum_{i < j, ij \text{ bonded}} \frac{k}{2} [r_{ij} - r_0]^2$$

non-bonded				bonded	
	Thio-Thio	Full-Full	Thio-Full		Thio-Thio
ϵ [eV]	0.115	0.277	0.178	k	300
σ [nm]	0.385	1.1	0.74	r_0 [nm]	0.14
Source	DFT	DFT	*	Source	**

Figure 2: Lennard-Jones chain model and parameters. Thiophene-thiophene (thio-thio) and fullerene-fullerene (full-full) parameters found in density functional theory literature [2,3]. * Thiophene-fullerene parameters σ and ϵ were calculated from the arithmetic and geometric mean, respectively, between thiophene-thiophene and fullerene-fullerene parameters. ** Equilibrium bond distance r_0 , and spring constant k , estimated from an effective conjugation coordination model [4].

evolve using the velocity verlet integrator algorithm with an MD timestep of $\Delta t = .001$ for 4000 steps. During this equilibration period, velocity rescaling occurred every 100 steps to achieve the target temperature. At the end of the equilibration period, the kinetic energy was reset based on the average total energy calculated throughout the equilibration period. Finally, after equilibration, production runs of Time=100, $\Delta t = .001$ were performed with velocity rescaling turned off to preserve NVE dynamics (fig. 3).

Based on optimal experimental solar concentration (1:1 wt:wt polymer:fullerene) and cell dimensions (100nm thick over a $\sim 2 \text{ cm}^2$ area), the number density was estimated to be $\rho = N/L^3 = 2$, with 1 in every 4 molecules being a fullerene; therefore, simulations took place under periodic boundary conditions in a cubic box of length $L \sim 5 \text{ nm}$ with 60 fullerene molecules and 180 thiophene monomers (chain length = 2, 4, 10, 20, 40, 60). To understand room temperature and “annealing” conditions, simulations took place at $T = 1$ and $T = 1.5$, respectively. To investigate fullerene phase separation during the annealing process, radial distribution functions for fullerene were measured before and after the production run for the $T=1.5$, $M=60$ case (fig.4). The ending configuration shows a second nearest neighbor peak nearly double in intensity from the starting configuration, suggesting a slight packing of fullerenes during the annealing process.

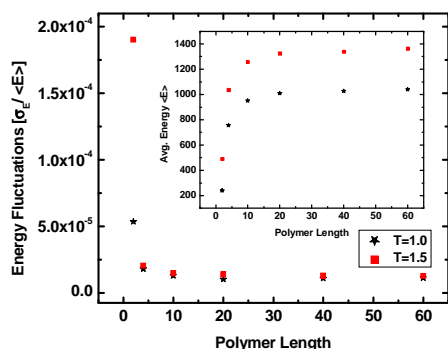


Figure 3: Energy conservation and fluctuations during a production run as a function of polymer length.

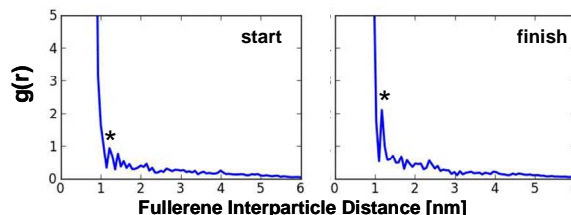


Figure 4: Fullerene radial distribution functions, $g(r)$, before and after a production run for $T=1.5$, $M=60$. The * denotes the second nearest neighbor peak. The radial distribution function was estimated by histogramming the interparticle fullerene distances into 100 bins.

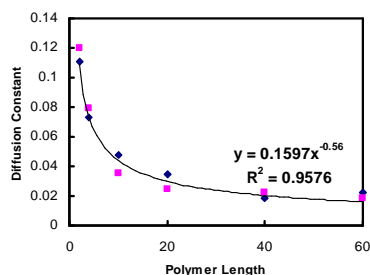


Figure 5: Thiophene diffusion constant as a function of polymer length for two different production runs ($T=1$). Despite the presence of fullerene molecules, thiophene diffusion followed a power law relationship.

Finally, to investigate the dynamics of the system, mean squared displacements were measured and used to calculate diffusion constants for the fullerene and thiophene molecules. Fullerene diffusion appeared to be invariant with polymer chain length, but thiophene diffusion followed a power law relationship (fig. 5). These results, especially the radial distribution functions, support experimental evidence from x-ray scattering and TEM tomography that phase separation does occur on a very small length scale even for relatively low temperature short anneals [5]. One fundamental limitation of this study is the fact that the fullerene and thiophene molecules are modeled with the same mass, masking the true dynamics of the system.

The mass of the fullerene molecule is roughly 6 times the thiophene mass. Adding more molecules and increasing the polymer length would improve the simulation as well. This study focused on polymers with length 2-60; however, typical polymers used in OPVs have about 300 monomer units, larger than the entire ensemble shown here. Finally, the simulation could be expanded to include functional groups on the thiophene monomers and fullerenes. Such functional groups are added to increase the solubility of the parent molecules and can greatly perturb the molecular packing, especially in dense films.

[1] S. H. Park, A. Roy, S. Beaupre, S. Cho, N. Coates, J. S. Moon, D. Moses, M. Leclerc, K. Lee, and A. J. Heeger, *Nat. Photonics* **3**, 297 (2009).

[2] Xie et al. Structure and sources of disorder in poly(3-hexylthiophene) crystals investigated by density functional calculations with van der Waals interactions. *Phys. Rev. B* (2011) vol. 83 (18) pp. 184117

[3] Girifalco et al. Carbon nanotubes, buckyballs, ropes, and a universal graphitic potential. *Phys Rev B* (2000) vol. 62 (19) pp. 13104-13110

[4] EHRENDORFER and KARPEN. THEORETICAL VIBRATIONAL-SPECTRA OF A BIPOLARONIC DEFECT IN OLIGOTHIOPHENES AND IN POLYTHIOPHENE - A COMBINED SEMIEMPIRICAL AND AB-INITIO STUDY. *J Phys Chem-Us* (1995) vol. 99 (15) pp. 5341-5353

[5] Treat et al. Interdiffusion of PCBM and P3HT reveals miscibility in a photovoltaically active blend. *Adv. Energy Mater.* (2011)