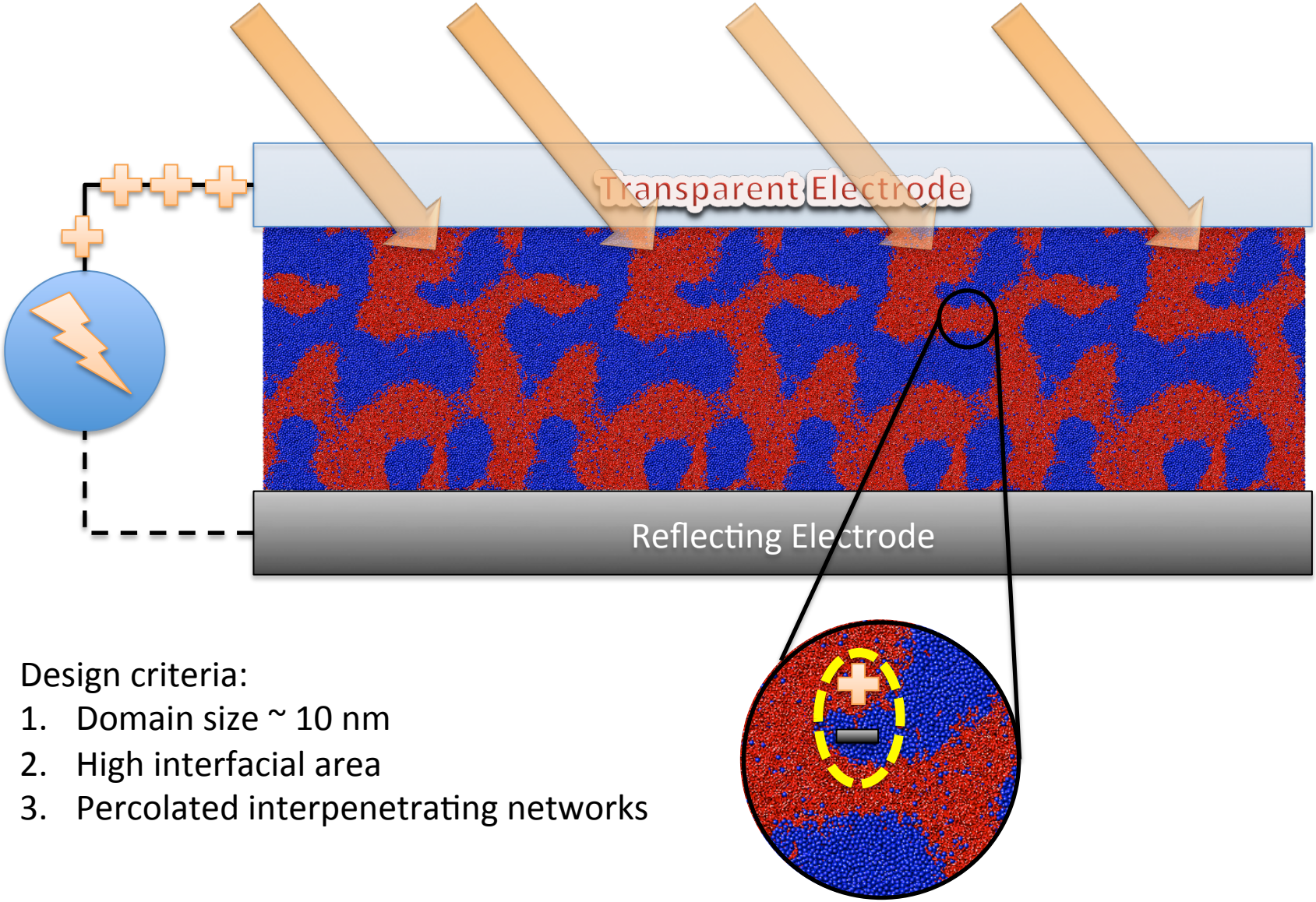
# Coarse-Grained Molecular Dynamics Simulations of Thermal Annealing of P3HT:PCBM Bulk Heterojunctions for Organic Photovoltaic Applications

Jan-Michael Y. Carrillo[a], Rajeev Kumar[b,c], Monojoy Goswami[b,c], Bobby G. Sumpter[b,c] and W. Mike Brown[a]

[a]National Center for Computational Sciences
[b]Center for Nanophase Materials Sciences
[c]Computer Science and Mathematics Division
Oak Ridge National Laboratory

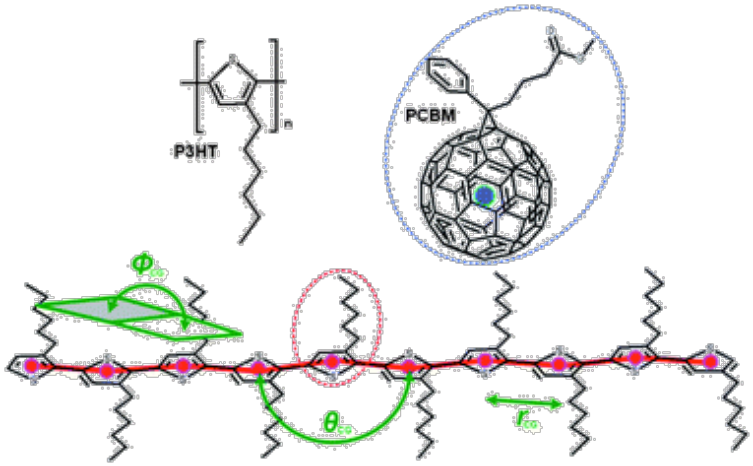
# Bulk Heterojunction Architecture (BHJ)

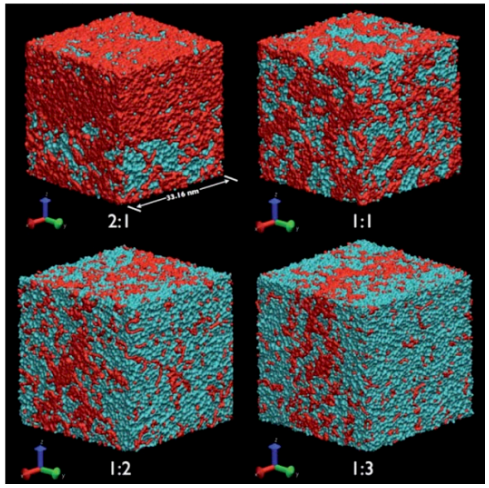



Design criteria:

1. Domain size ~ 10 nm
2. High interfacial area
3. Percolated interpenetrating networks

# Coarse-Grained Model




Lee, Pao and Chu. Energy Environ. Sci., 2011, 4, 4124-4132

Harmonic Bond Potential

$$U_{\text{bond}} = \frac{1}{2} k_{\text{b}} (r_{ij} - r_0)^2$$

OPLS Dihedral Potential

$$U_{\text{dihedral}} = \frac{1}{2} V_1 (1 + \cos\phi) + \frac{1}{2} V_2 (1 - \cos 2\phi) + \frac{1}{2} V_3 (1 + \cos 3\phi)$$

Harmonic Angle Potential

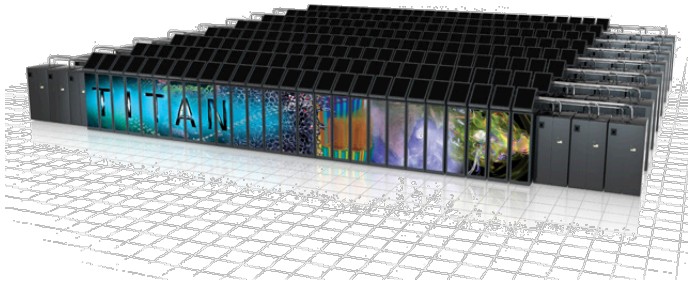
$$U_{\text{angle}} = \frac{1}{2} k_\theta (\theta_{jik} - \theta_0)^2$$

LJ Pairwise Potential

$$U_{\text{vdw}} = 4\varepsilon \left[ \left( \frac{\sigma}{r^{ij}} \right)^{12} - \left( \frac{\sigma}{r^{ij}} \right)^{6} \right]$$

# System Sizes

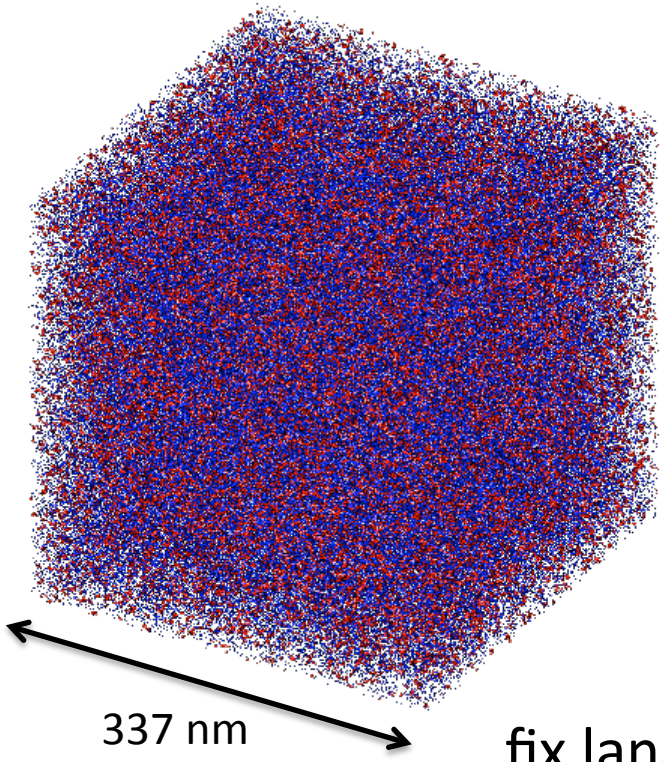
| | m | N | L (nm) | $N_{P3HT}$ | $N_{PCBM}$ | $N_{TOTAL}$ |
|---|---|---|---|---|---|---|
| $\phi_m = 0.25$ | 32,400 | 100 | 127 | 3,240,000 | 1,776,150 | 5,016,150 |
| $\phi_m = 0.33$ | 32,400 | 100 | 115 | 3,240,000 | 1,182,916 | 4,422,916 |
| $\phi_m = 0.50$ | 32,400 | 100 | 100 | 3,240,000 | 591,458 | 3,831,458 |
| $\phi_m = 0.67$ | 32,400 | 100 | 90 | 3,240,000 | 295,729 | 3,535,729 |

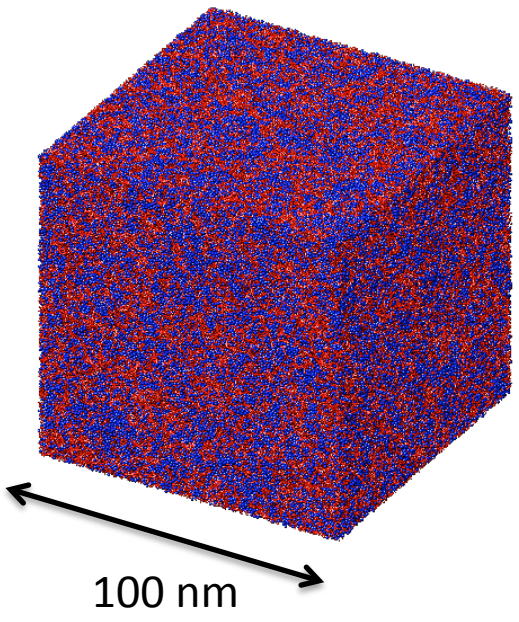


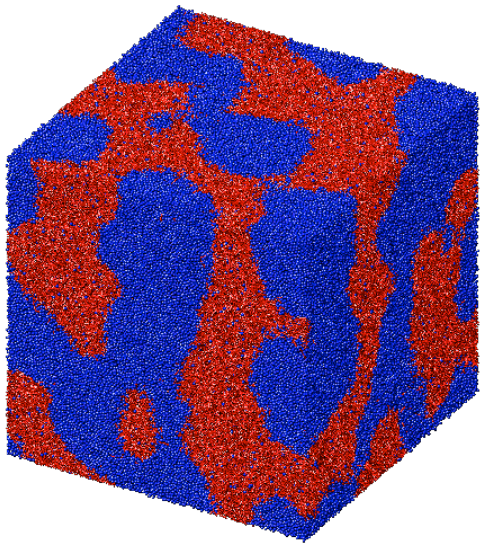

- 11% Capacity of Titan
- Ran up to 400 ns
- Box size ~ 100 nm
  - The same order as experiments

N: Length of the degree of polymerization of the conductive polymer, P3HT.
m: Number of P3HT chains.
$\phi_{m:}$: Weight fraction of P3HT in the P3HT:PCBM system.
L: Dimensions of the simulation box where the volume of the box is L x L x L.
$N_{P3HT}$: Number of P3HT beads.
$N_{PCBM}$ : Number of PCBM beads.
$N_{TOTAL}$: Total number of beads.

# Simulation Protocol



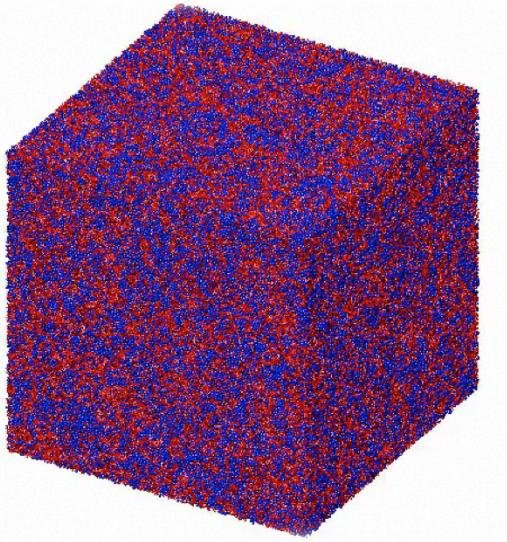



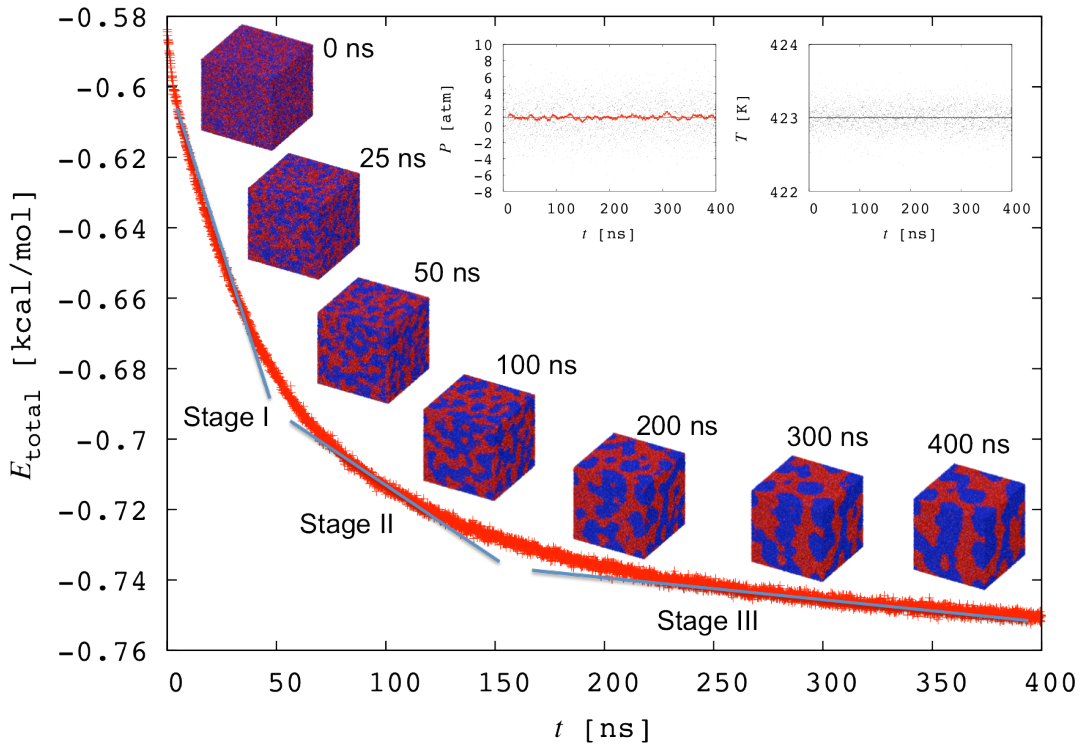
fix langevin
fix deform
fix nve

fix npt (1 atm and 423 K)
package gpu
400 ns
3456 cpu-cores
216 gpu's or nodes

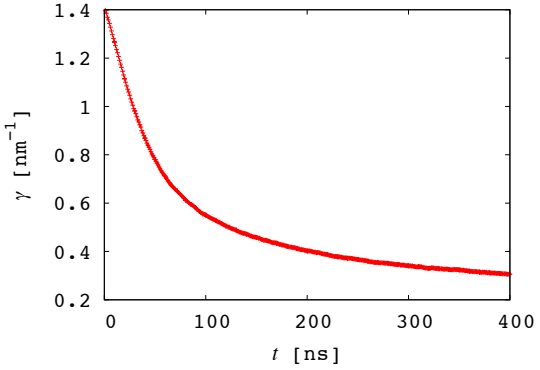
**Images were created using dump image*

# Simulation Results






Interface area to volume ratio

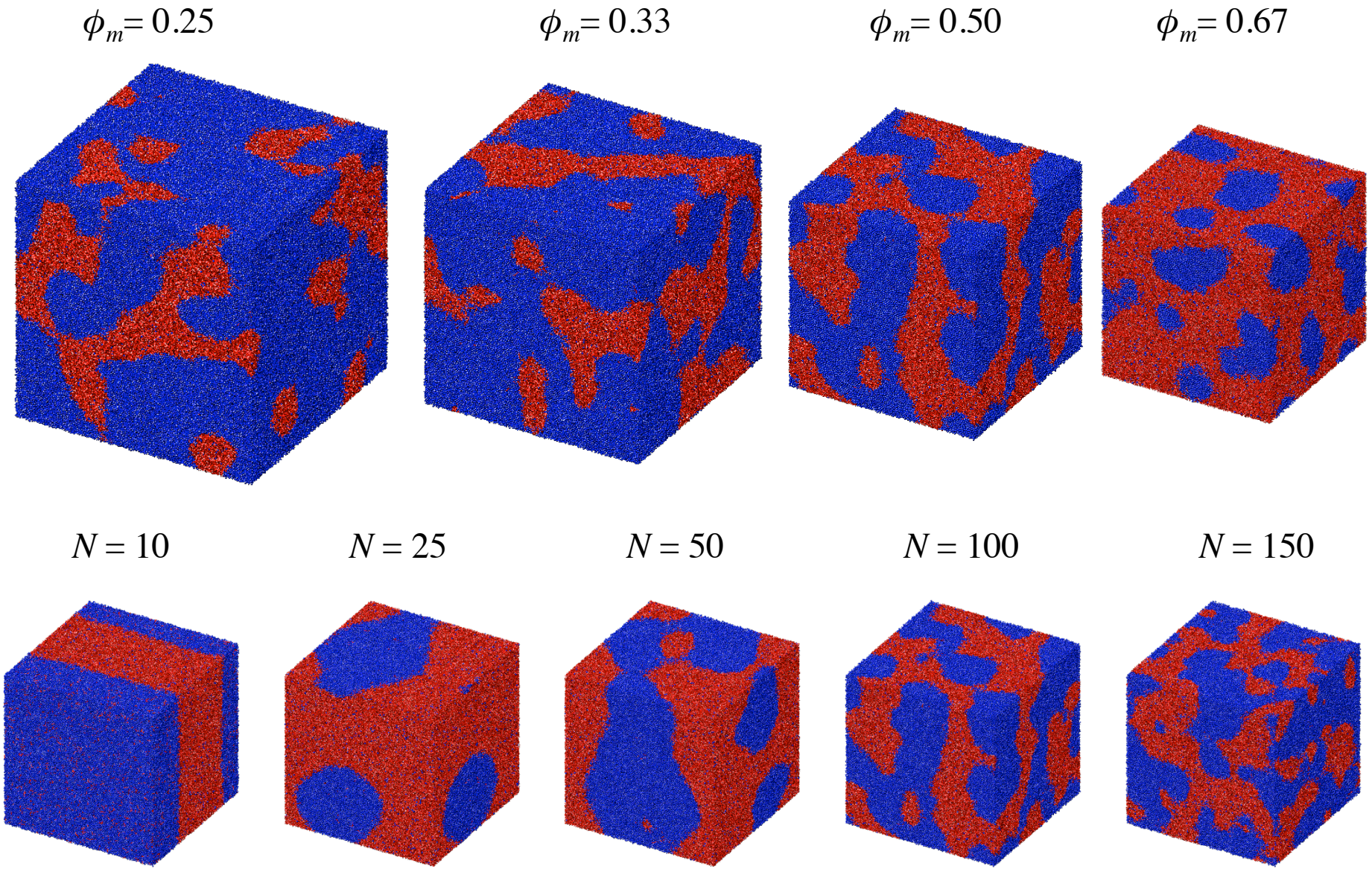



T = 423 ± 0.71 K

P = 1.06 ± 2.21 atm

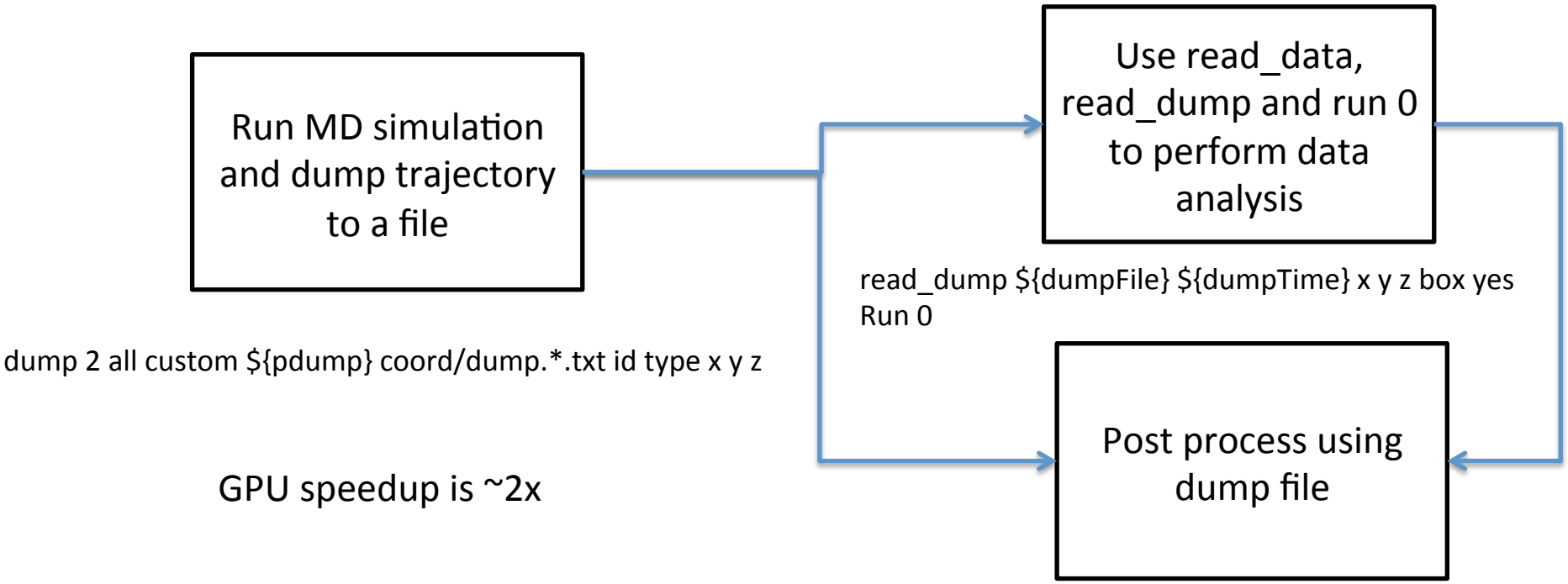
**movie created from dump image and ffmpeg*

# Simulation Results



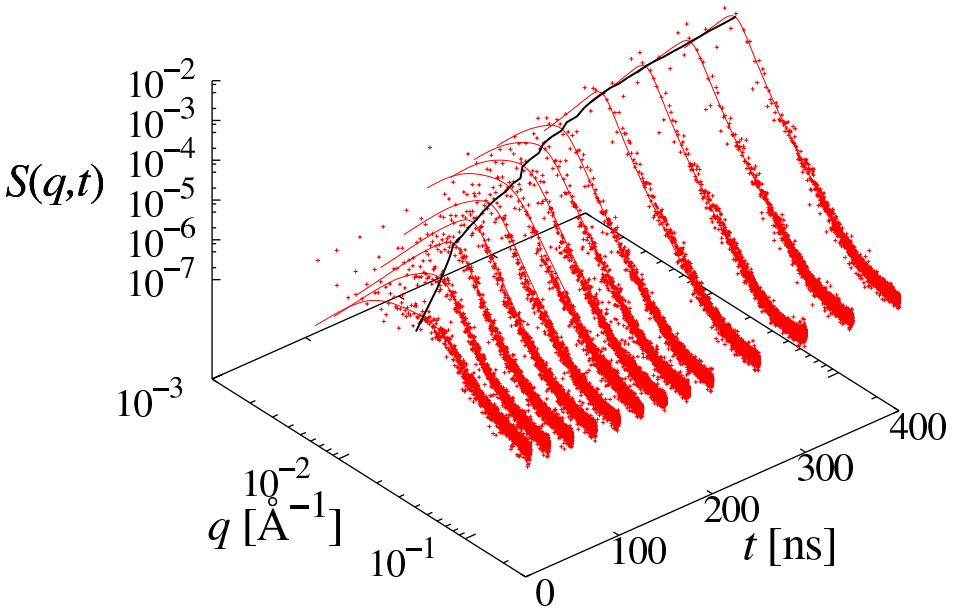
# Data Analysis

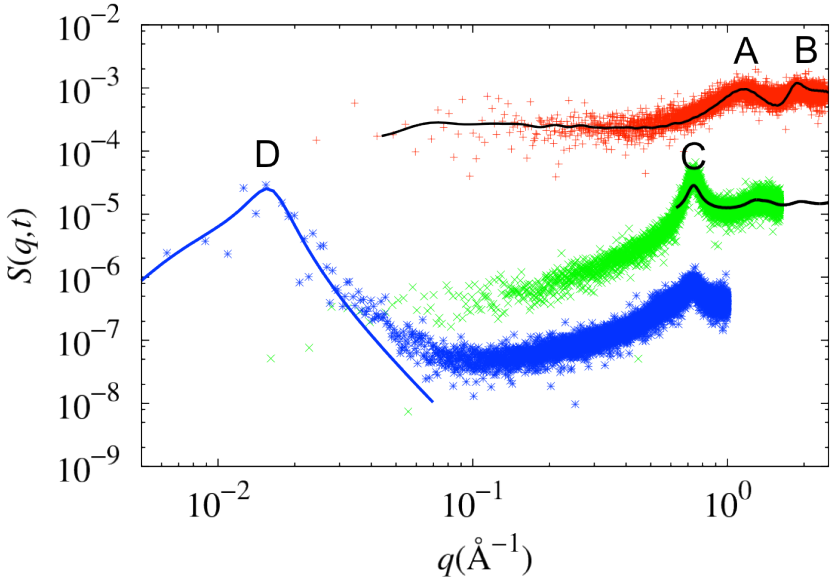
- Structure factor, $S(q,t)$
- Average local packing fraction, $\eta$
- Interface area to volume ratio, $\gamma$

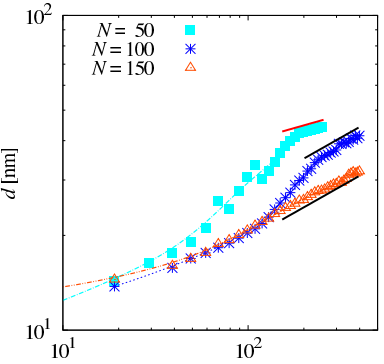


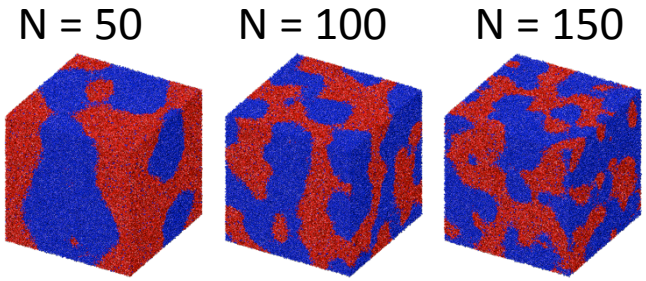
# Domain Size

fix ave/spatial to form a 3D density grid of the P3HT beads
Take the FFT of the 3D grid to get $S(q_l,q_m,q_n)$




RED : neat P3HT
GREEN : neat PCBM
BLUE : P3HT:PCBM

# Miscibility of PCBM in P3HT

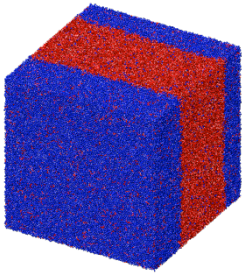
## Persistence Length of P3HT polymer

$$b_K = \frac{b}{\cos(\theta_0/2)} \frac{1+\cos(\theta_0)}{1-\cos(\theta_0)} \frac{1+\langle\cos(\phi)\rangle}{1-\langle\cos(\phi)\rangle} = 75.7\text{Å}$$

$$l_p = \frac{b_K}{2} = 37.8\text{Å} \sim 10 \text{ P3HT beads}$$

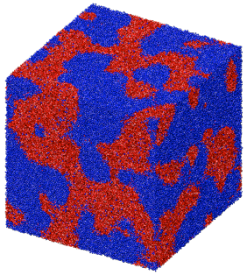
Rod-Like

$N = 10$

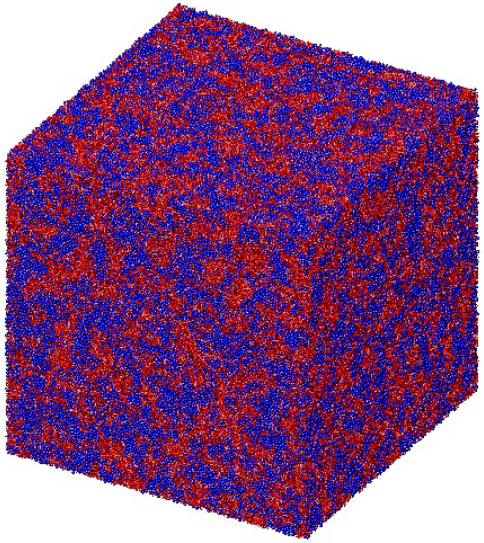


Coil-Like

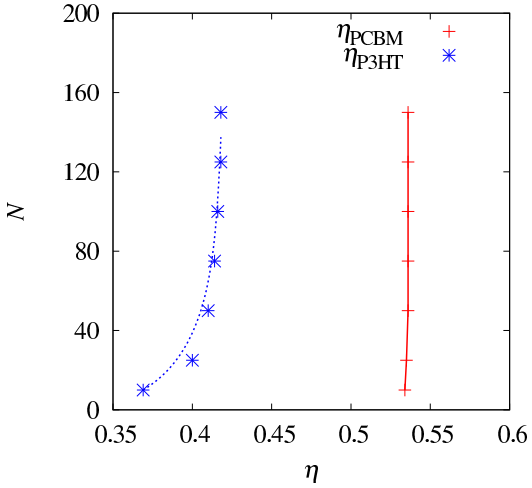
$N = 150$



Evolution of N=10



## Packing fractoin, $\eta$



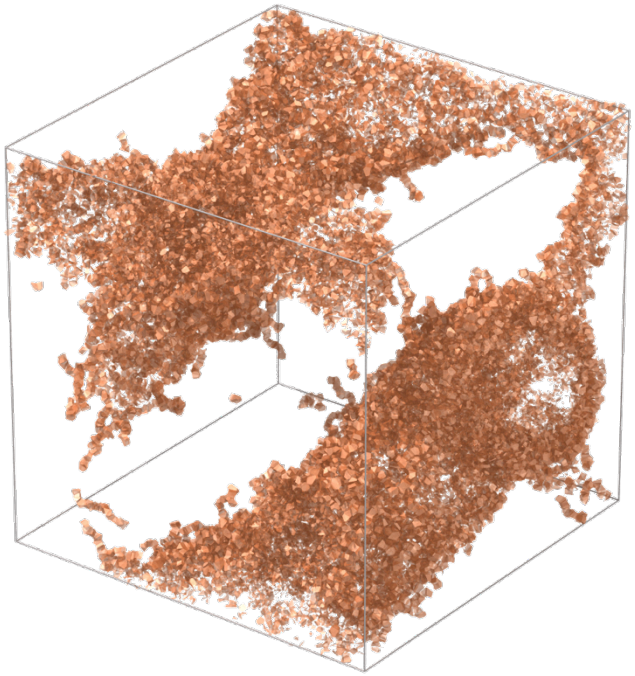

## Flory χ parameter

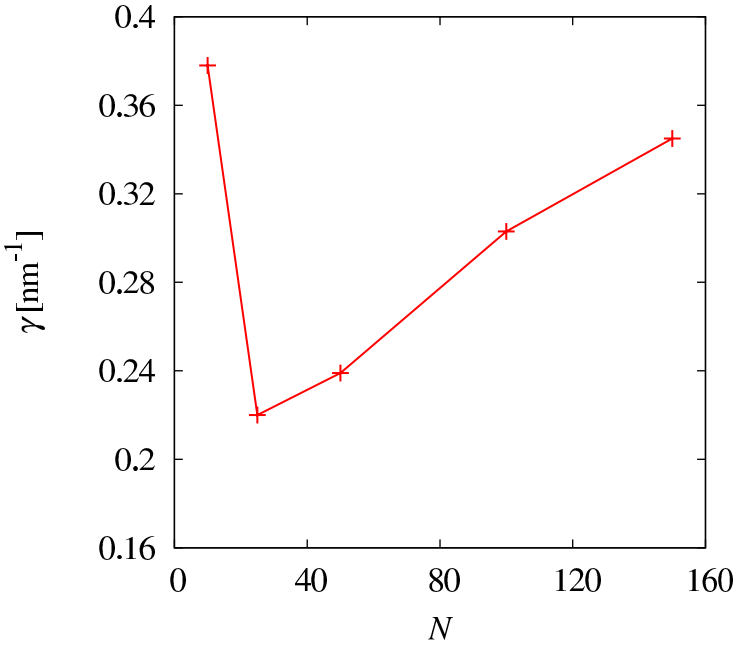
$$\Delta U_{\text{mix}} = \chi \phi_v (1-\phi_v) kT$$

$$\chi = 0.92 \pm 0.1$$

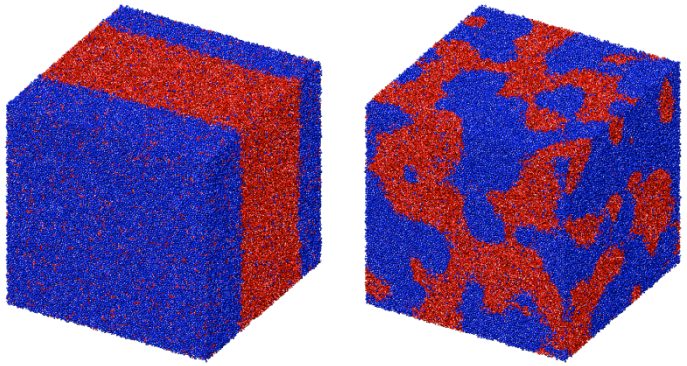
# Interface Area to Volume Ratio, $\gamma$

Radical Voronoi Tesselation
using Voro++



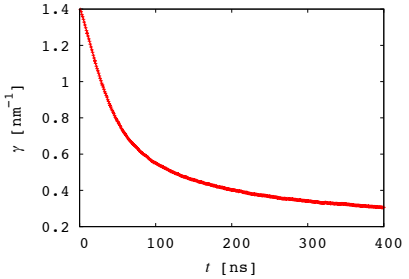



$N = 10$ $N = 150$



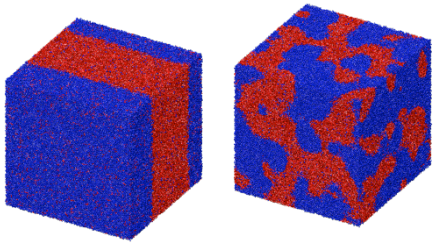
# Summary

1. It is important to choose the correct time scale and length scale in the simulation of donor and acceptor blends in OPV's




2. At constant P3HT weight percent, We observed different morphologies at different P3HT chain lengths.

3. These different morphologies are stabilized by the different conformational entropies of rod-like vs. coil-like chains and short chains vs. long chain.



4. With all the Titan nodes already available, future work includes systems with substrates or addition of compatibilizers

**This work is currently under review at PCCP.*

# Acknowledgements




This research was conducted in part under the auspices of the Office of Advanced Scientific Computing Research, Office of Science, U.S. Department of Energy under Contract No. DE-AC05-00OR22725 with UT-Battelle, LLC. This research used resources of the Leadership Computing Facility at Oak Ridge National Laboratory, which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC05-00OR22725 with UT-Battelle, LLC.