Thermodynamics

Chemical Engineering @ Tongji University

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Introduction

Every scientific discipline has its characteristic set of problems and systematic methods for obtaining their solution - that is, its paradigm.

The Structure of Scientific Revolutions

Thomas S. Kuhn,

There are four steps in evolution, scientific discovery

Revolution, developing new paradigm
Normal science, studies inside paradigm
Anomalies
Crisis

Chemical engineering started @MIT in 1888

The first paradigm was proposed by Arthur D. Little in 1915, based on the unifying concept of "unit operation“

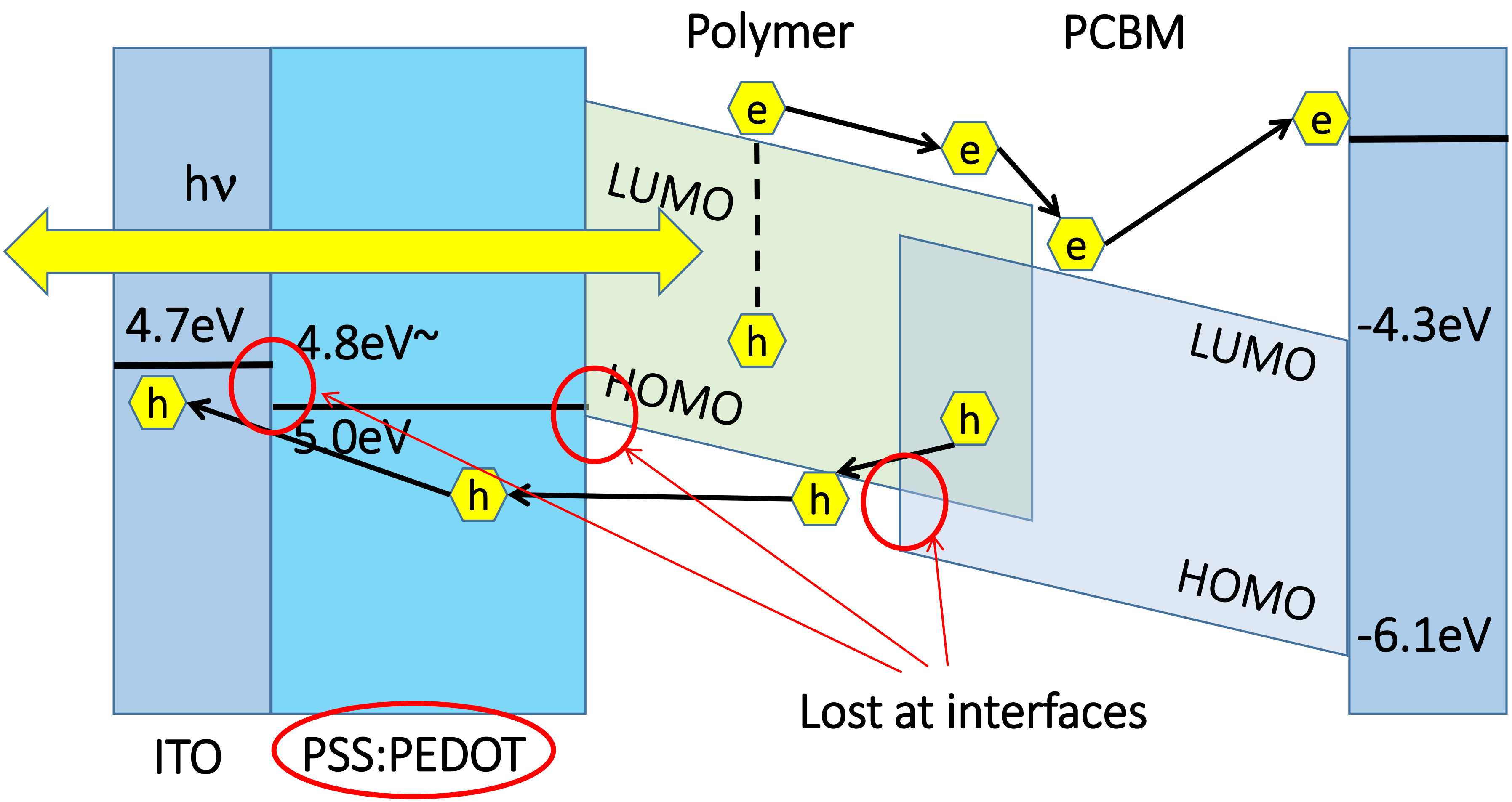
The “old” traditional paradigm around 1950, including: thermodynamics and kinetics, transport phenomena, unit operations, reaction engineering, process design and control, and plant design and system engineering

Crisis-- explosion of new products and materials from the biotechnology industry, the electronics industry, or the high-performance materials industry "critically" dependent on **structure and design** at the **molecular level** for their usefulness

The "new" **traditional** paradigm started around 2000: make increasing use of computers, **artificial intelligence**, and expert systems in problem solving

Already 20 years old !

Organic Solar Cell / OLED



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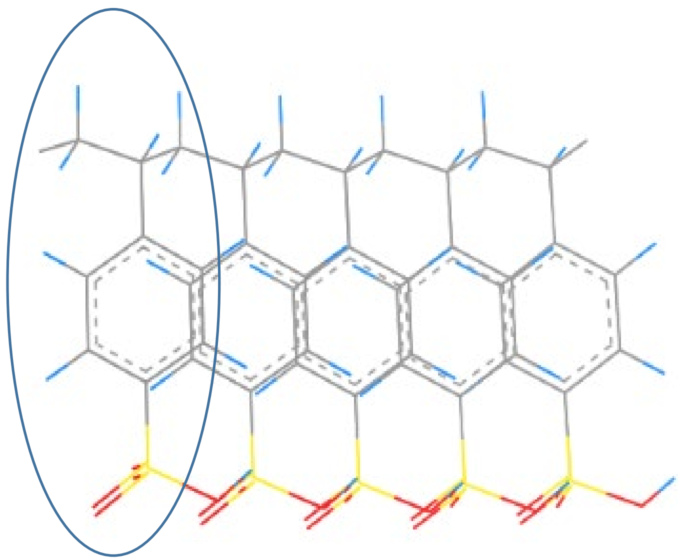
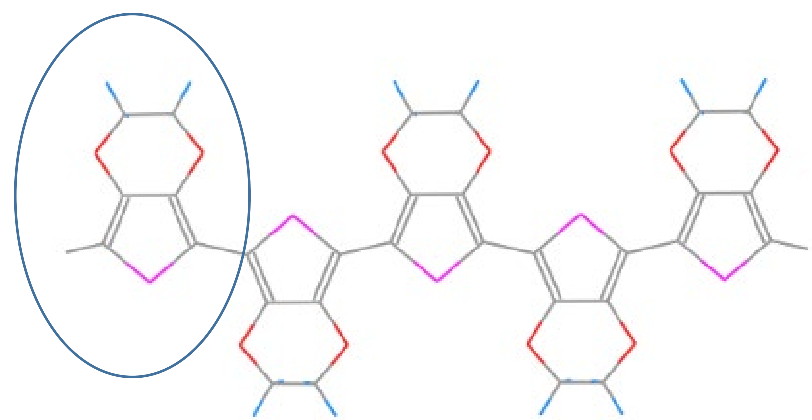
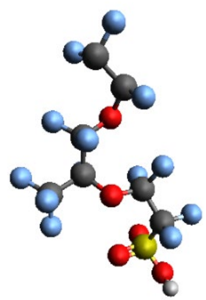
MODELS AND METHODS

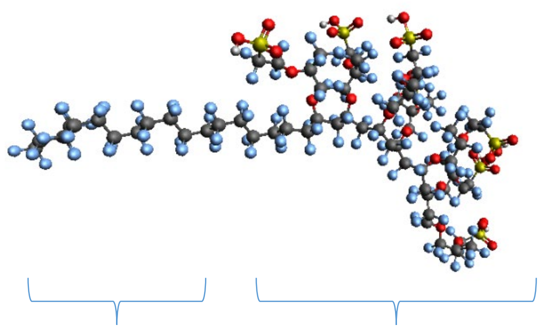
- **Monomers optimized using DFT, B3LYP, 6-311G++2p,2d**
- **Beads, Chain length and configurations**
  - **DPD beads representation of PEDOT and PSS**





PFI (Nafion) polymer





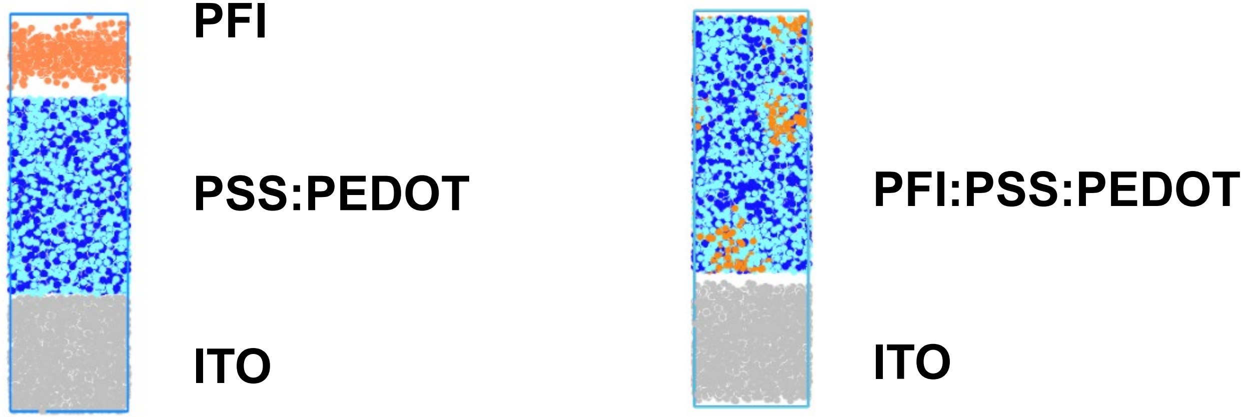
Hydrophobic Hydrophilic

$$-(CF_2\text{-}CF_2)_x-(CF_2\text{-}CF)_y-$$
$$|$$
$$(O\text{-}CF_2\text{-}CF)_m-(O\text{-}CF_2)_n-SO_3H$$
$$|$$
$$CF_3$$

T **M** **M** **N**

DPD simulation

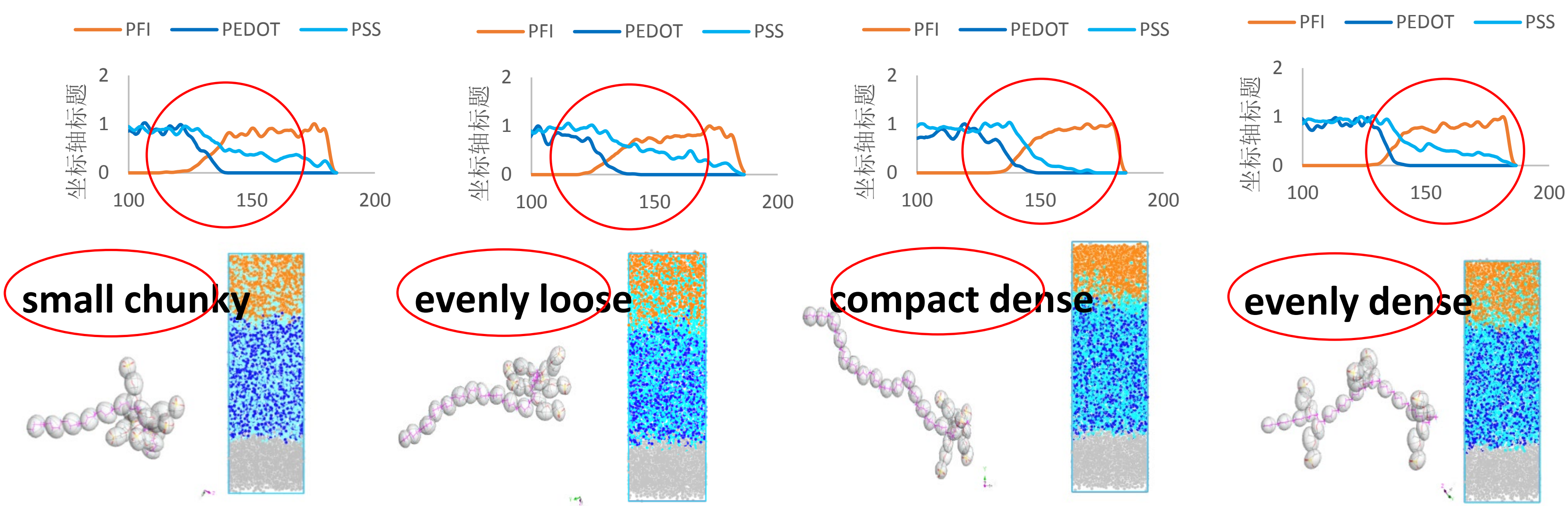
- **Initial conditions**
- **DPD Simulation box of PEDOT:PSS:PFI=1:2.5:0.5 @ room temperature**



Stacked Condition **Random Distribution Condition**

PFI structure configurations

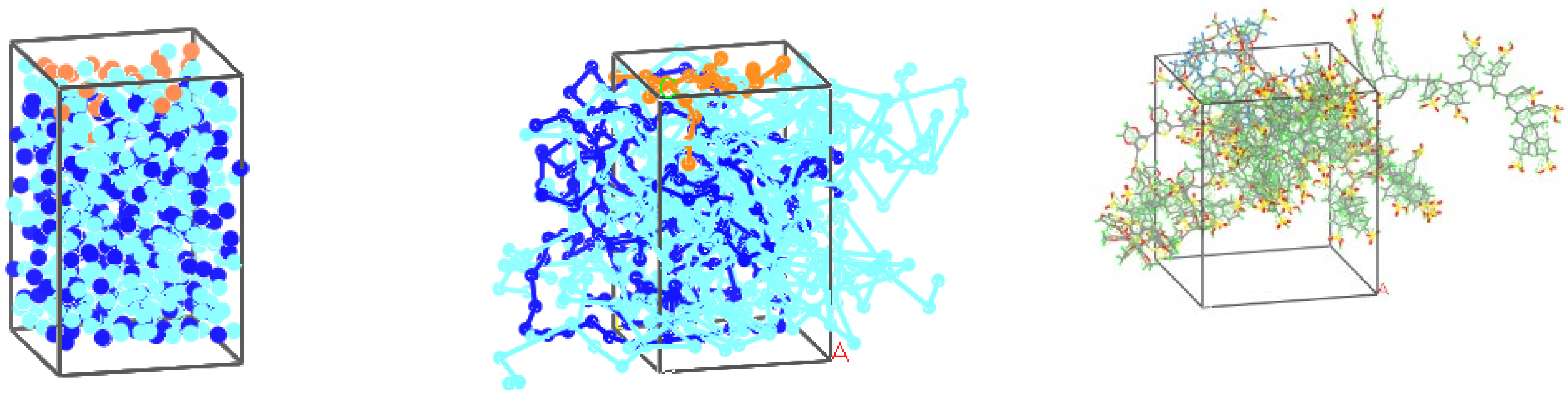
- **PEDOT:PSS:PFI=1:2.5:1.0 @RT**



$n_N > n_T$ **$n_N \sim n_T$** **$n_N < n_T$**

50%/3 **50%/3** **50%/3** **50%**

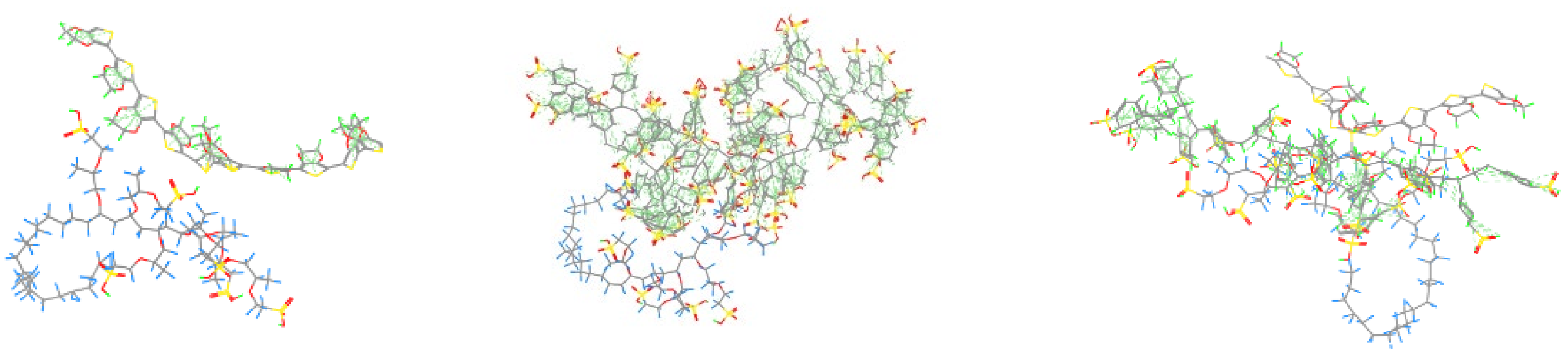
Mapping



a. DPD b. CG c. Atomistic

Figure 1. Mapping results of PSS:PEDOT:PFI; a DPD, b CG, c Atomistic(top portion)

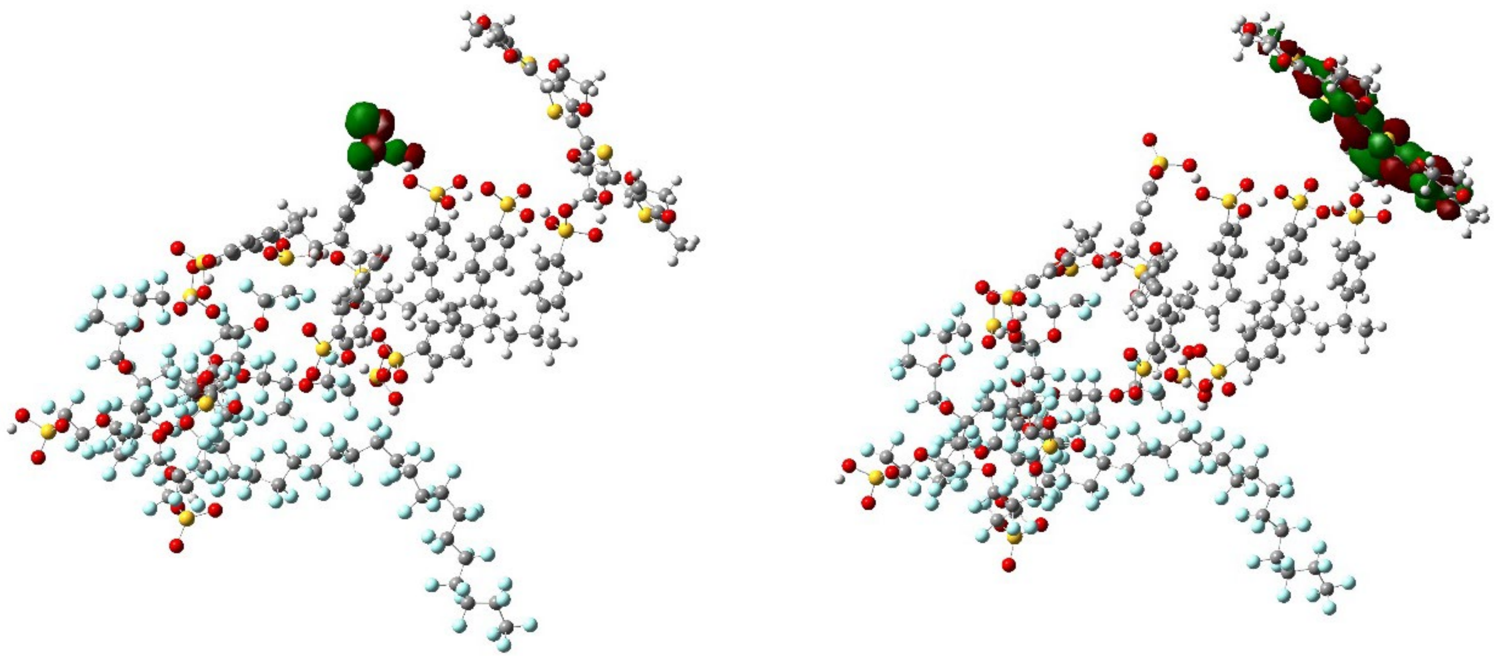
Mapping



PFI-PEDOT **PFI-PSS** **PFI-PSS-PEDOT**

Figure 2. Snapshots of PFI:PSS:PEDOT complex from DPD simulation mapping results.

PFI:PSS:PEDOT HOMO-LUMO



HOMO -5.35eV **LUMO**

Figure 5. Interactive energy [kcal/mol]of PSS:PEDOT=6:1 **and perovskite crystal**

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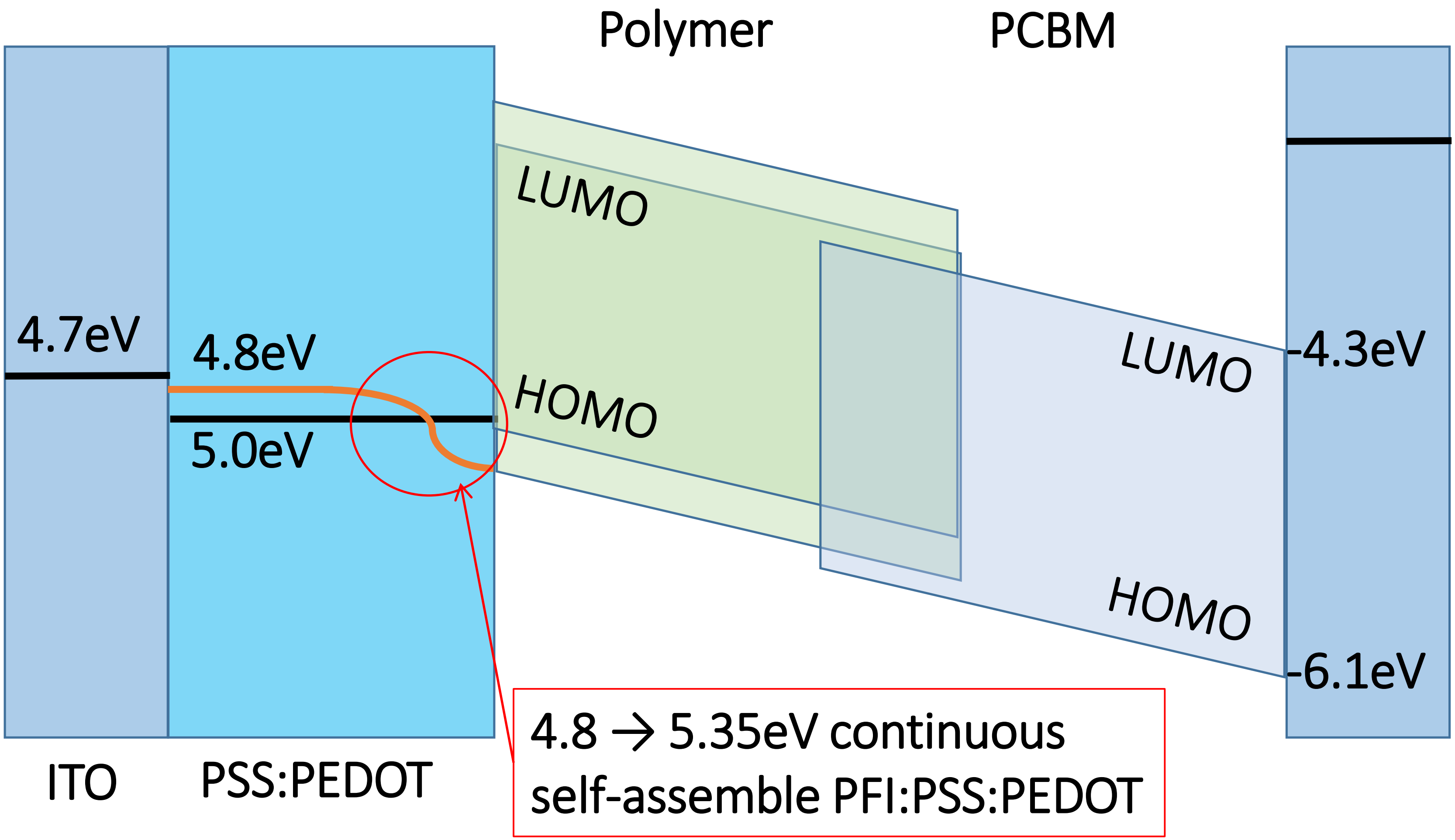


New problem arises: conductivity

So we ask siri what to do: Siri, how to increase conductivity ?

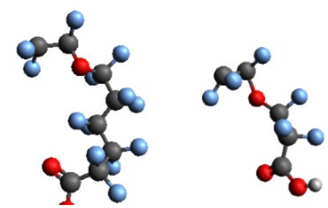
- **PSS:PEDOT:PFI, PSS:PEDOT:NiOx micro phase structures 2016**
- **PSS:PEDOT:PFI, work function 2017**
- **PSS:PEDOT:solvent, micro phase structures 2018**
- **All agree well with the experiment results.**

- **In this contribution,**

  predict PSS:PEDOT:Flemion micro structure

  to test Model-Based-Reasoning

Flemion polymer

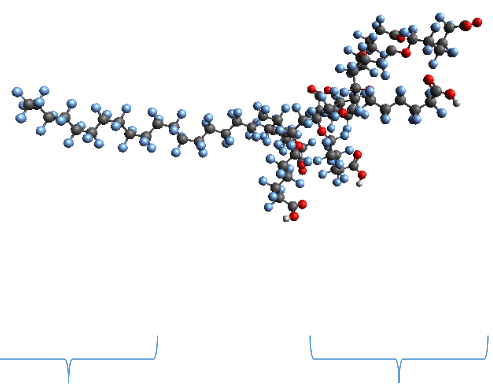


$$—(CF_2\text{-}CF_2\text{-}CF_2)_x—(CF_2\text{-}CF)_y—$$

$$|$$

$$(O—CF_2)—(CF_2\text{- }CF_2\text{-- }CF_2\text{-}CF_2)—COOH$$

T M T F



Hydroforbic Hydrophilic

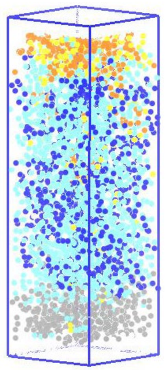
$$—(CF_2\text{-}CF_2\text{-}CF_2)_x—(CF_2\text{-}CF)_y—$$

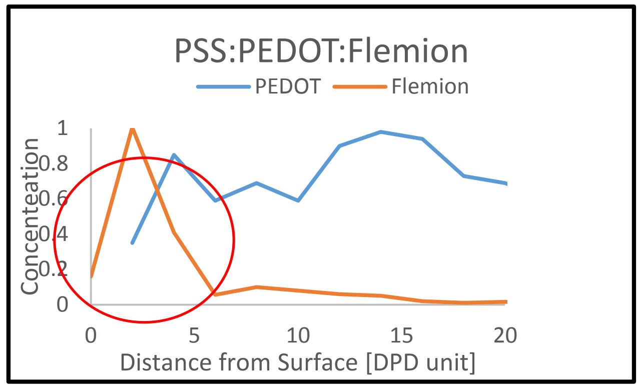
$$|$$

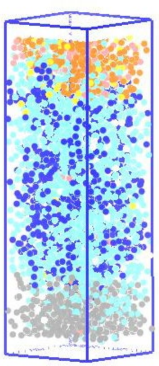
(O—CF2)-CF2)—COOH

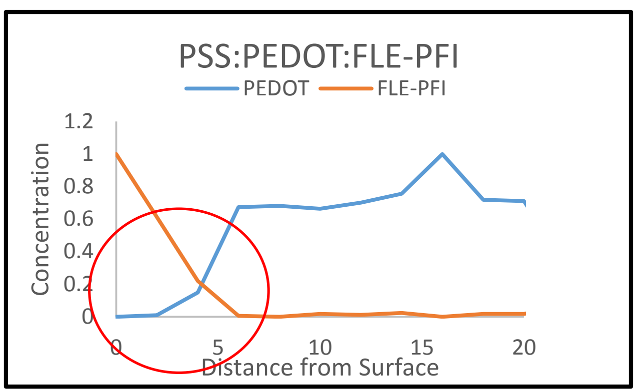
T M F

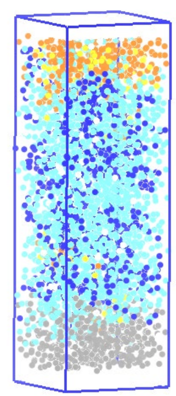
DPD Results

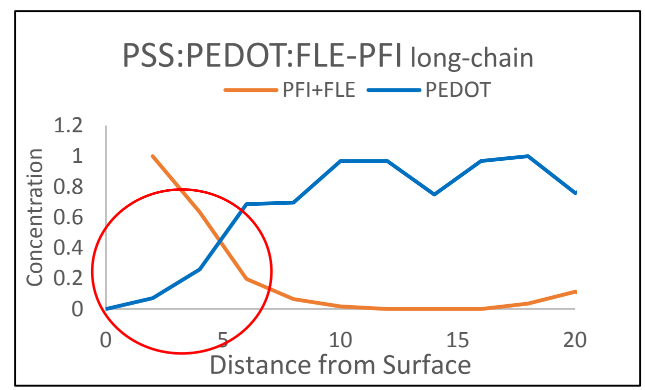



PSS:PEDOT:Flemion
PEDOT
Flemion
Concenteation
0
0.2
0.4
0.6
0.8
1
0
5
10
15
20
Distance from Surface [DPD unit]

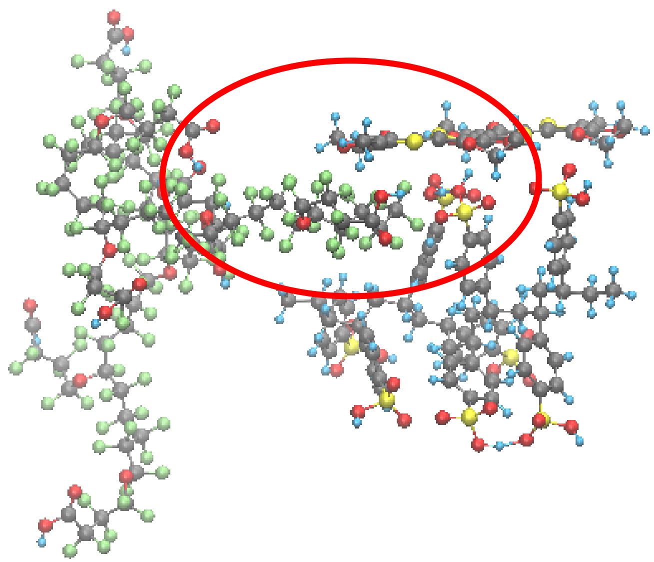



PSS:PEDOT:FLE-PFI
PEDOT
FLE-PFI
Concentration
0
0.2
0.4
0.6
0.8
1
1.2
0
5
10
15
20
Distance from Surface

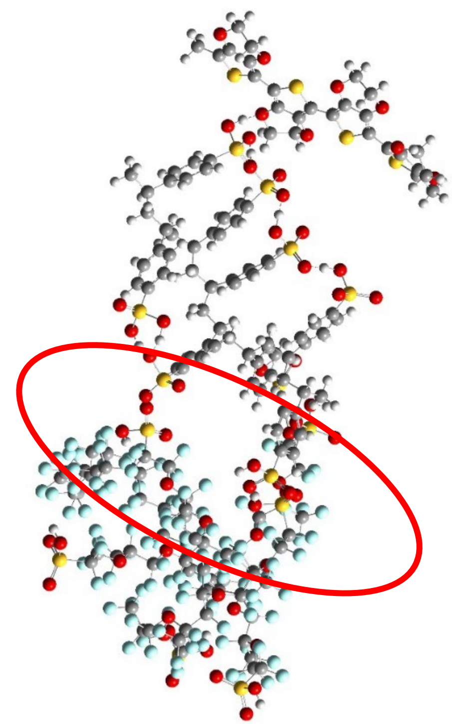



PSS:PEDOT:FLE-PFI long-chain
PFI+FLE
PEDOT
Concentration
0
0.2
0.4
0.6
0.8
1
1.2
0
5
10
15
20
Distance from Surface

DFT configuration optimization results



PSS:PEDOT:Fle (2019)



PSS:PEDOT:PFI (2017)

Why is this has anything to do with thermodynamics ?

- **Classical Molecular Dynamics: very small in size and time duration**
- **Mesoscale bridging microscopic view to scales in real life**
- **Dissipative particle dynamics (DPD)—Coarse grain + Flory-Huggins theory a branch of solution theory in thermodynamics**

$$\left(\frac{\Delta G_{mix}}{RT}\right)\left(\frac{V_r}{V}\right) = \frac{\phi_A}{N_A}\ln\phi_A + \frac{\phi_B}{N_B}\ln\phi_B + \chi_{AB}\phi_A\phi_B$$

$$\chi_{AB} = \chi^{FH}$$

<— Regular Solution

Interaction: non - bonding + bonding

Entropy of mix, ideal solution **Enthalpy of mix** **Entropy of mix**

Thermodynamics is neither engineering, nor physics, nor chemistry, nor biology.
It is a tool used by all above and taken by all science and engineering students.
Thermodynamics occupies the same place in sciences as logic in humanities.

The origin

- The term “thermodynamics” was introduced by Lord Kelvin himself to direct attention to the dynamic nature of heat and to contrast this perspective with previous conceptions of heat as a type of Fluid.
- When taken literally, thermodynamics implies a field concerned with the mechanical action produced by heat.

the Science of Heat

In ancient west, Earth, Water, Air and Fire are the generally known and often quoted ancient elements of nature (Aristotle added Aether as the 5th, the quintessence (精髓))

- In China, we have 土木火水金.
- By the end of the 18th century, French rich aristocrat chemist Lavoisier advocated a theory explaining that the phenomena involving the transfer of heat are the result of a weightless fluid substance, he called “caloric.”

- **This "caloric," as Lavoisier assumed, permeated the gaps between atoms of a solid causing thermal expansion and whose loss through the surface could explain Newtonian cooling.**
- **Count (伯爵) Rumford found that heat can be produced by the boring of cannons and one can generate "unlimited amount" of heat simply by keeping boring the cannon—mechanical to heat**
- **Count Rumford's opinion eventually prevailed, but not after Lavoisier being severed by a Guillotine.**

Bulk vs. individual particles

Newtonian's physics deals with individual point mass, position and momentum

Thermodynamics deals with bulk properties, P,V; T,S

In probability and statistics, we learned individual events may occur in sequential or parallel fashion

Events independently more than 20, maybe described using normal distribution

When events piling up, central value theorem tells us, the distribution becomes Gaussian.

Following steepest decent, expand about its maximum value, which occurs at <E>

$$\ln P(E) = \ln P(E) + \delta E \left.\frac{\partial \ln P(E)}{\partial E}\right|_{\langle E\rangle} + \frac{1}{2}(\delta E)^2 \left.\frac{\partial^2 \ln P(E)}{\partial E^2}\right|_{\langle E\rangle} + \cdots$$

where the second term equals 0, since has a maximum at <E>; for the third term let,

$$\left.\frac{\partial^2 \ln P(E)}{\partial E^2}\right|_{\langle E\rangle} = \left.\frac{\partial^2 \ln(\ln \Omega - \beta E)}{\partial E^2}\right|_{\langle E\rangle} = \left.\frac{\partial^2 \ln \ln \Omega}{\partial E^2}\right|_{\langle E\rangle}$$

Refer to my PPT in Teaching--> Grad --> Statistical Mechanics

$$P(E_1, E_2) = \frac{\int_{E_1}^{E_2} \Omega(E')dE'}{\int_{E_0}^{\infty} \Omega(E')dE'}$$

Substitute <E> as E,

$$\left.\frac{\partial^2 \ln P(E)}{\partial E^2}\right|_{\langle E\rangle} = \frac{\partial}{\partial\langle E\rangle}\left(\frac{\partial \ln \ln \Omega(\langle E\rangle)}{\partial\langle E\rangle}\right) = \frac{\partial\beta}{\partial\langle E\rangle}$$

$$= -\frac{1}{k_B T^2}\frac{\partial T}{\partial\langle E\rangle} = -\frac{1}{k_B T^2 C_V}$$

$$P(E) = \exp\left[-\frac{(E-\langle E\rangle)^2}{2k_B T^2 C_V}\right]$$

For $\delta E = 10^{-6}\langle E\rangle,\ N = 10^{21}$**, using** $\langle E\rangle = 3/2Nk_B T,\ C_V = 3/2Nk_B$

$$P(E)/P(\langle E\rangle) = e^{-10^9}$$

$$E \sim N \qquad \Delta E \sim \sqrt{N} \qquad |\Delta E / E| << 1$$

the probability of finding particles outside <E> decreases drastically as N increases which allows the states in thermodynamics be defined with very few vriables, while the fluctuations at microscopic level still exist.