# Physical Aspects of Polymer-Carbon Nanotube Interactions with MD Simulations and Visual-Analytic Tools


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**Funding:**

*Free software (VMD, LAMMPS, PackMol)*





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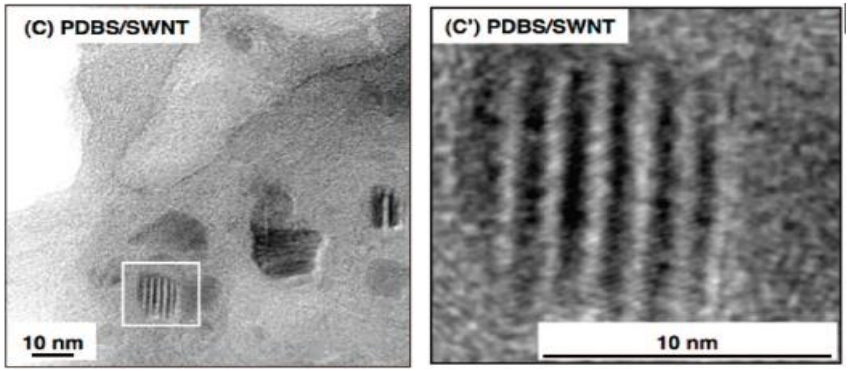
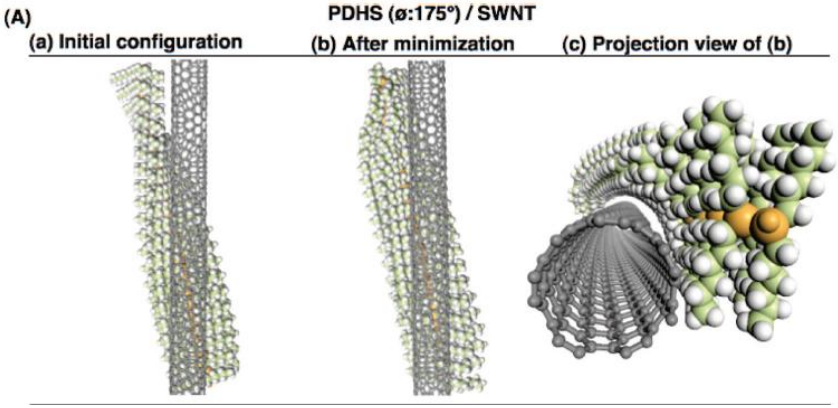
# Non-Covalent Interactions with Polymers and CNTs




*M Naito, K Nobusawa, H Onouchi, M Nakamura, K-I Yasui, A Ikeda and M Fujiki; JACS 2008, 130 (49), 16697*




**Presence of CNTs can impact properties of the material:**

- Toughness
- Mechanical strength
- Crystalline morphology
- Conductivity
- Biocompatibility

**Interaction depends on:**

Structure and functionalization of CNTs

Structure of polymeric surroundings

Interfacial interactions between the polymer chains and CNTs

**Polymer "wrapping" can be utilized to:**

- Solubilize CNTs
- Effectively disperse the nanotube reinforcement in the matrix of a nanocomposite
- Alter the properties of the material

# RESULTS: Polymer-CNTs in Vacuum

Syamal Tallury

PPE

PA

PPV

PPY

PET

PP

PAN

PEO

PS

PLA

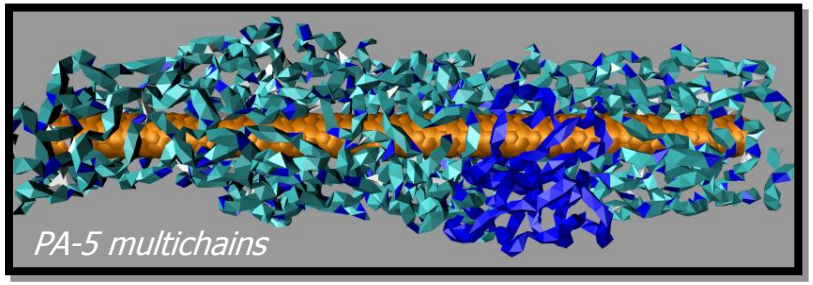
PCL

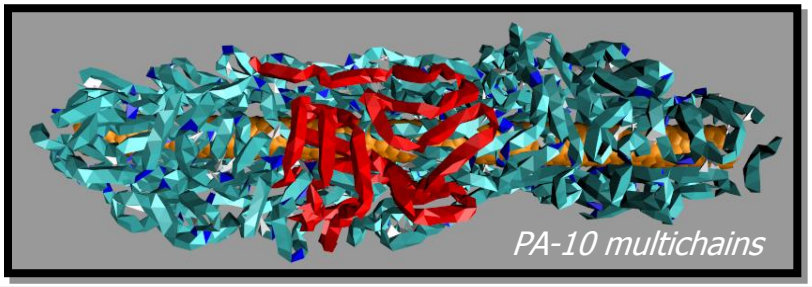
N6

PMMA

SS Tallury and MA Pasquinelli, JPCB 114(12): 4122–4129 (2010); JPCB 114(29): 9349–9355 (2010).

# Visual-Analytic Tools for Particle Simulation Data

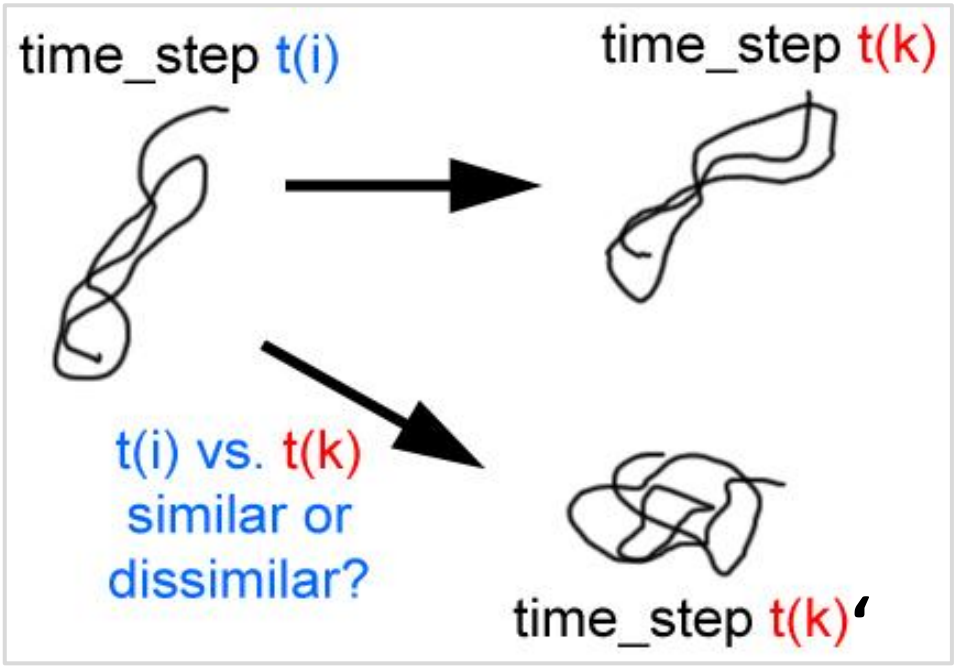



- **Observe structure-property relationships**
  - Among polymer molecules of same type and different types
- **Identify patterns in spatial and temporal trajectories**
  - Could provide insight into properties of interest, for instance the induction of polymer crystallization within an amorphous media
- **Explore relationships among system parameters**
  - Understand what dictates the dynamics of the interfacial interactions of polymer-nanoparticle
- **Provide a tool for making rational choices about system parameters**
  - To improve the microstructure and the macroscopic properties of a material by tuning quantities such as the chemical composition or processing conditions

SA Thakur and MA Pasquinelli, *Macromolecular Theory and Simulations* (2011) 20(4): 286-298. SA Thakur, SA Thakur, SS Tallury, MA Pasquinelli, and TM Rhyne, in *Advances in Visual Computing* (2009) 129-139.

# Basic Approach




Comparing polymer conformations at distinct time steps

**Conformation** refers to the 3D structure of a polymer molecule in a single time step

C. Best and H.-C. Hege, "Visualizing and identifying conformational ensembles in molecular dynamics trajectories," Computing in Science and Engg., vol. 4, no. 3, pp. 68–75, 2002.

SA Thakur and MA Pasquinelli, *Macromolecular Theory and Simulations* (2011) 20(4): 286-298. SA Thakur, SA Thakur, SS Tallury, MA Pasquinelli, and TM Rhyne, in *Advances in Visual Computing* (2009) 129-139.

# Feature Vector

A feature vector encapsulates some property of a polymer conformation using a **numeric measure**.

Example of a numeric measure: **Atomic distances**

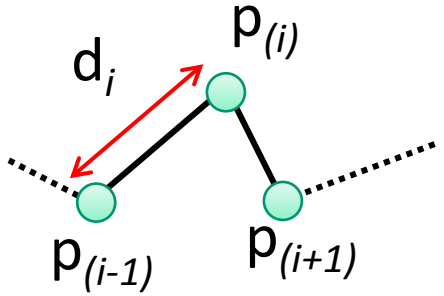
$$d_i = | \vec{p}_{(i+1)} - \vec{p}_{(i)} |$$

Feature vector

$$d_t = \{d_0, \ldots\ldots d_{N-1}\}$$

t = time step

[Best and Hege, 2002]

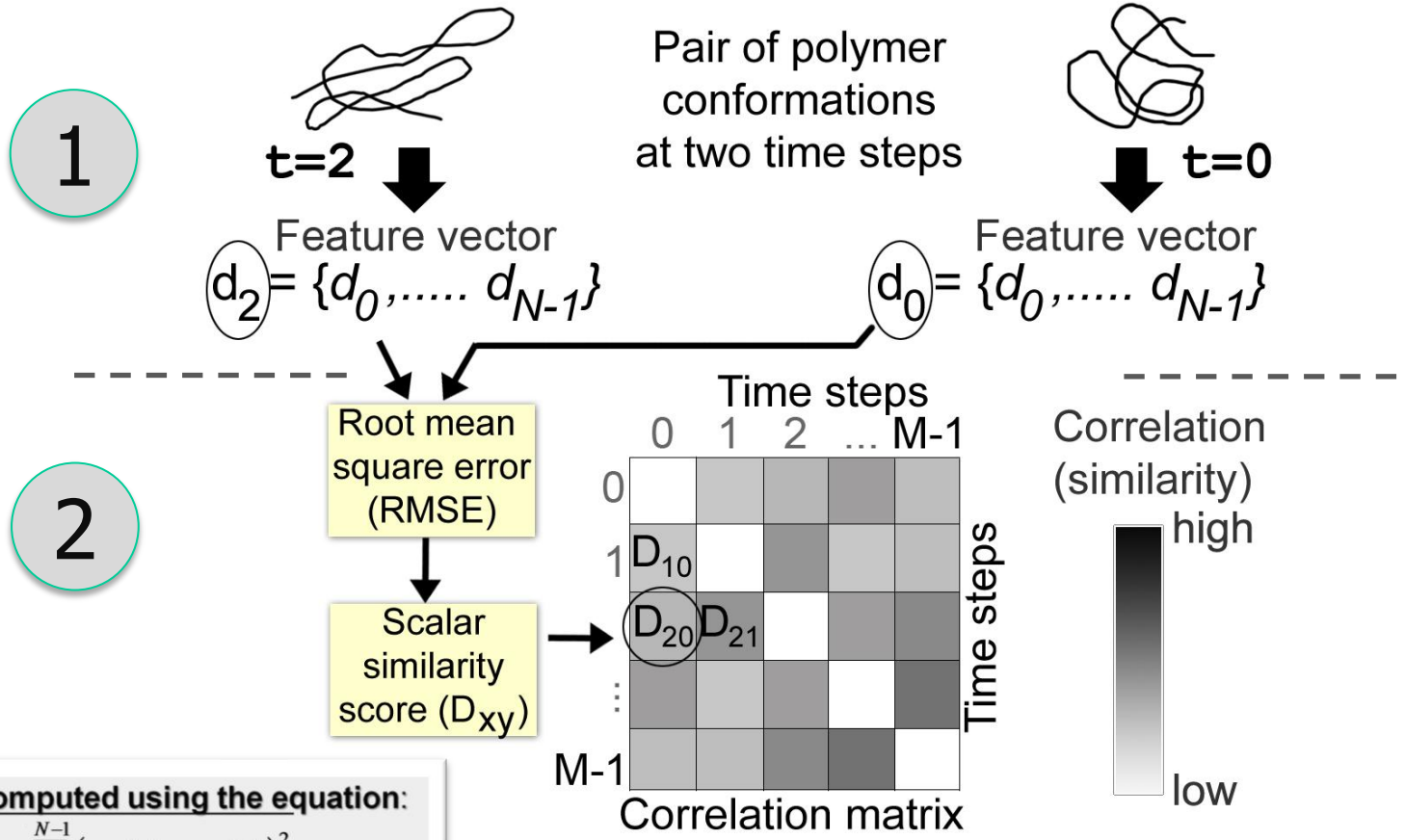



polymer backbone bonds and atoms at time step `t'

SA Thakur and MA Pasquinelli, *Macromolecular Theory and Simulations* (2011) 20(4): 286-298. SA Thakur, SA Thakur, SS Tallury, MA Pasquinelli, and TM Rhyne, in *Advances in Visual Computing* (2009) 129-139.

# Methodology

- Compute correlations of polymer conformations




**Pair-wise distances are computed using the equation:**

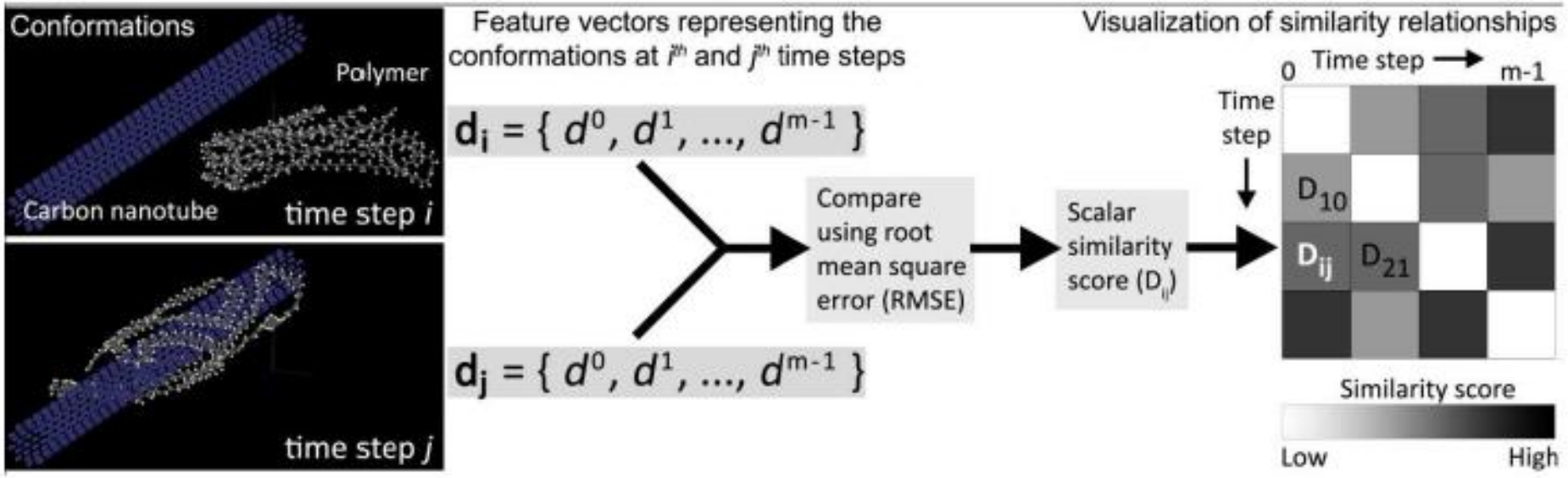
$$D_{xy} = 1 - \sqrt{\frac{2}{N(N-1)} \sum_{i=0}^{N-1} \left(d_x(i) - d_y(i)\right)^2}$$

*Where the pair $d_x(i)$ and $d_y(i)$ correspond to the elements of the feature vectors at time steps x and y from the MD simulations*

*Data is normalized relative to the largest RMSE*

SA Thakur and MA Pasquinelli, *Macromolecular Theory and Simulations* (2011) 20(4): 286-298. SA Thakur, SA Thakur, SS Tallury, MA Pasquinelli, and TM Rhyne, in *Advances in Visual Computing* (2009) 129-139.

# APPLICATION: Polymer-CNT Interactions

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# Examples of Numeric Metrics

## Inter-atomic (Euclidean) distances

Calculated between unique pairs of backbone atoms in a polymer conformation:

$$d_{Dist} = \left| R_i - R_j \right| \qquad \begin{matrix} i > j \\ i, j \in [0,N\text{-}1] \end{matrix}$$

## Bond vectors

Orientations of bonds along polymer backbone:

$$d_{ROG} = \left\{ \mathbf{v}_i = p_{i+1} - p_i \right\} \qquad i \in [0,N\text{-}1]$$

## Rotational moment of inertia

$$d_{RMI} = \left\{ d_i = m_i R_i^2 \right\} \qquad i \in [0,N\text{-}1]$$

## Radius of gyration

$$d_{ROG} = \left\{ d_i = R_i^2 \right\} \qquad i \in [0,N\text{-}1]$$

**Pair-wise distances are computed using the equation:**

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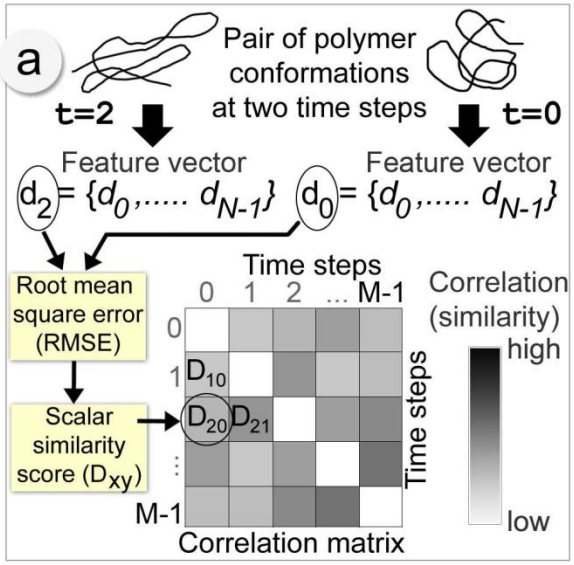
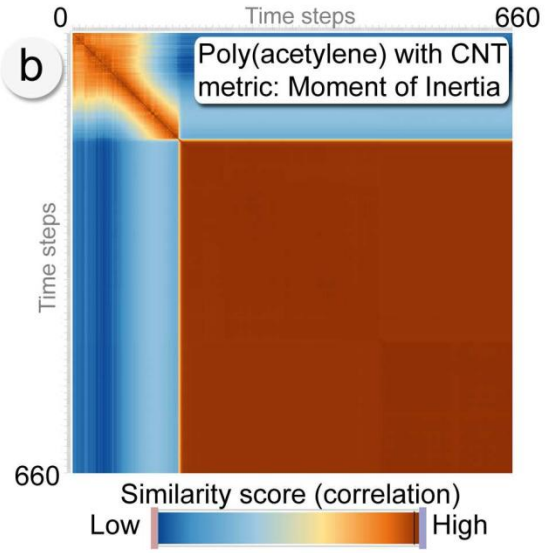
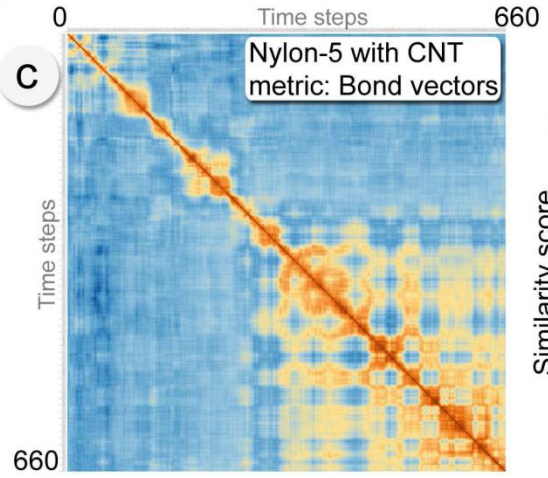
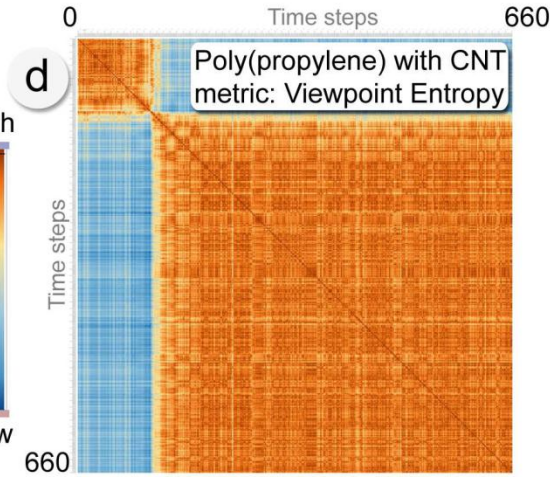
# Similarity Matrices with Different Numeric Metrics








*Data is normalized relative to the largest RMSE*

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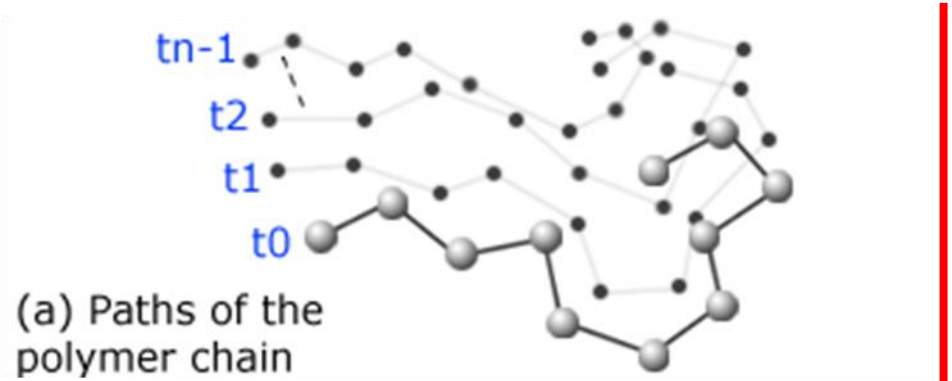
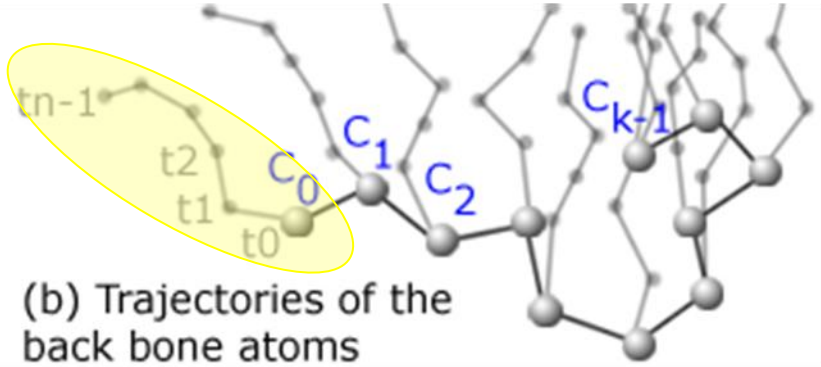
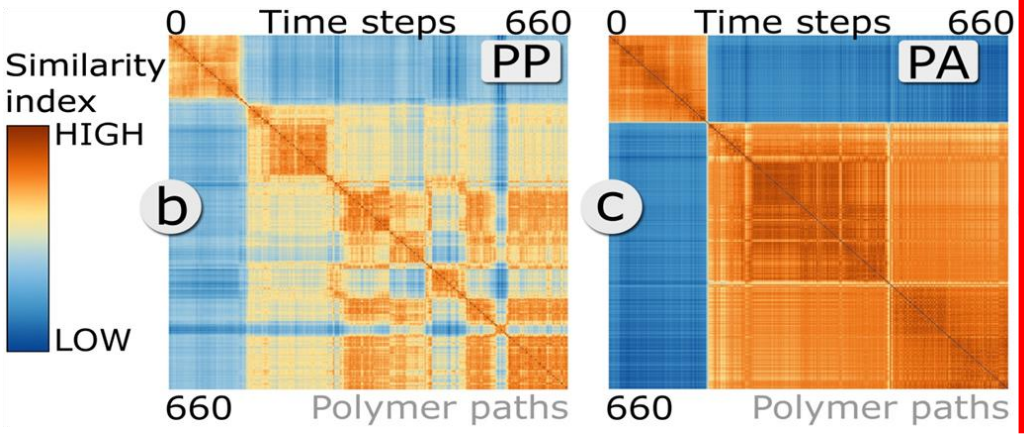
# Indeces for Similarity Matrices

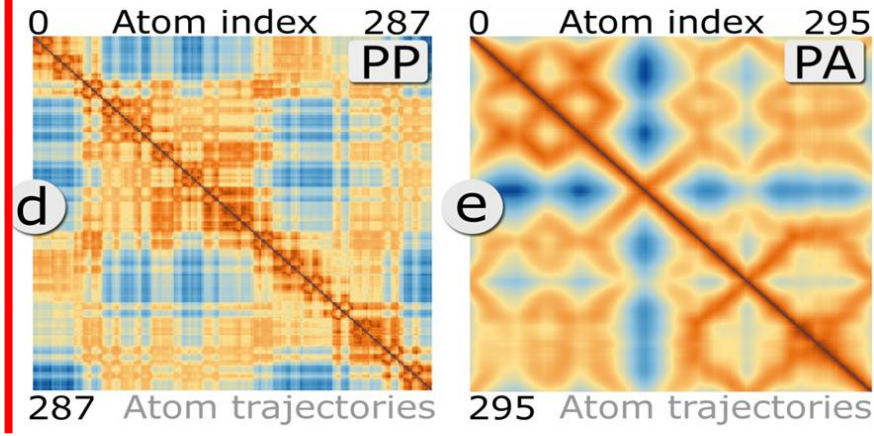


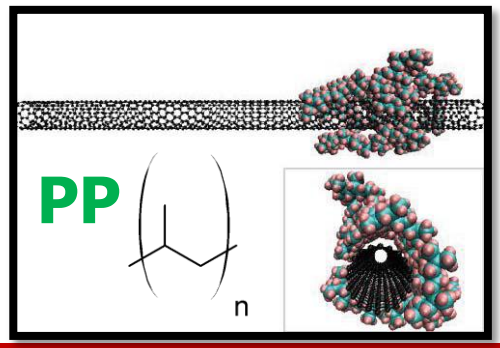

(a) Paths of the polymer chain

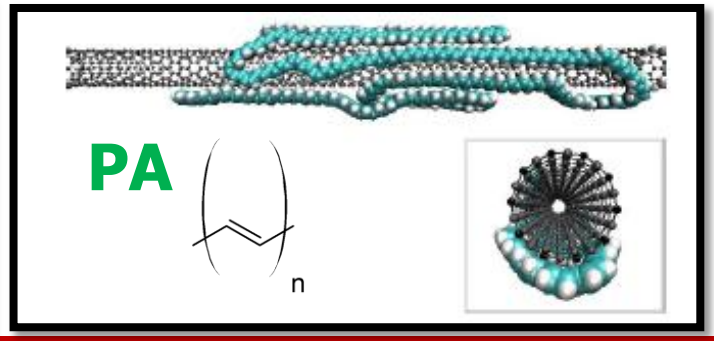



(b) Trajectories of the back bone atoms



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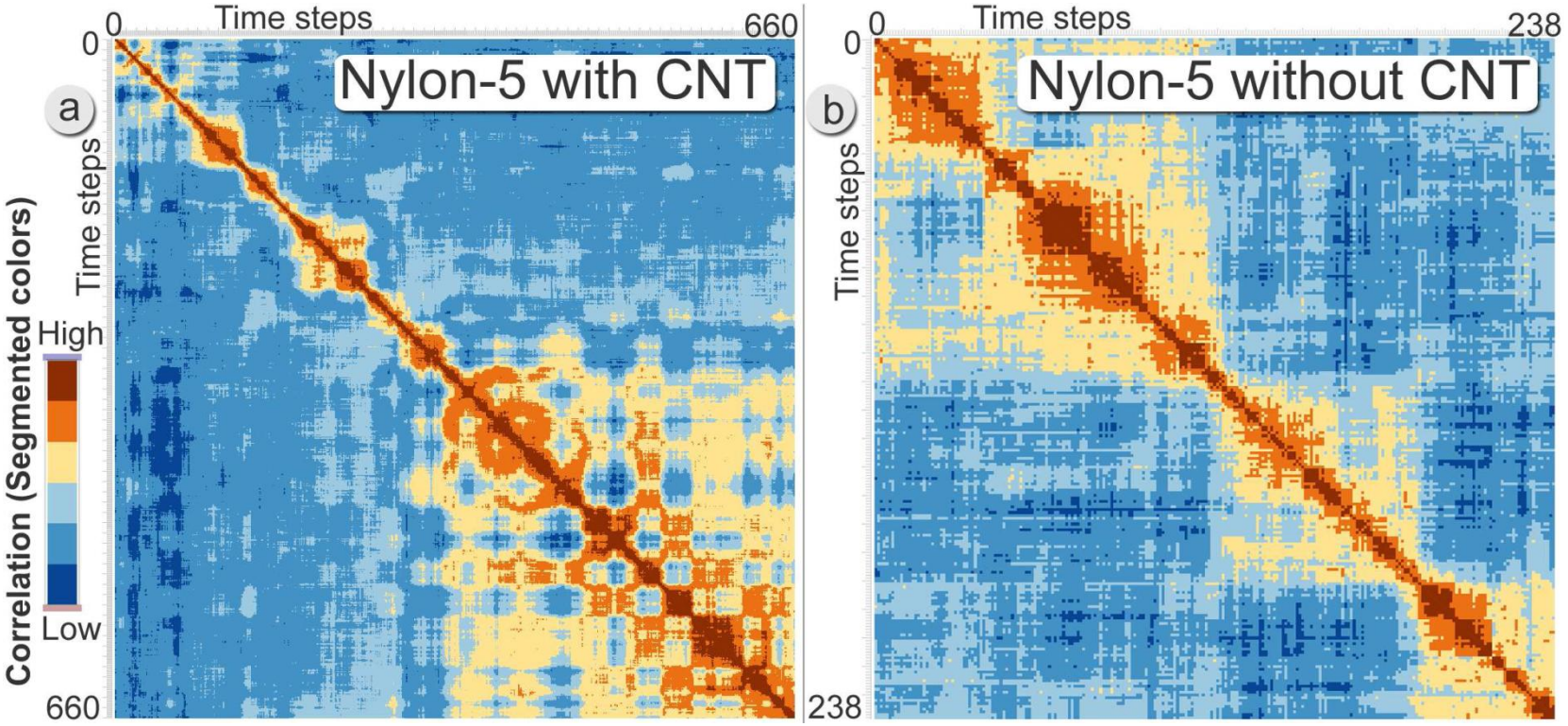


Matrices using a segmented color to display similarity relationships between conformations of Nylon-5 during an MD simulation in two distinct cases, namely (a) with a CNT, and (b) without a CNT.

*Data is normalized relative to the largest RMSE*

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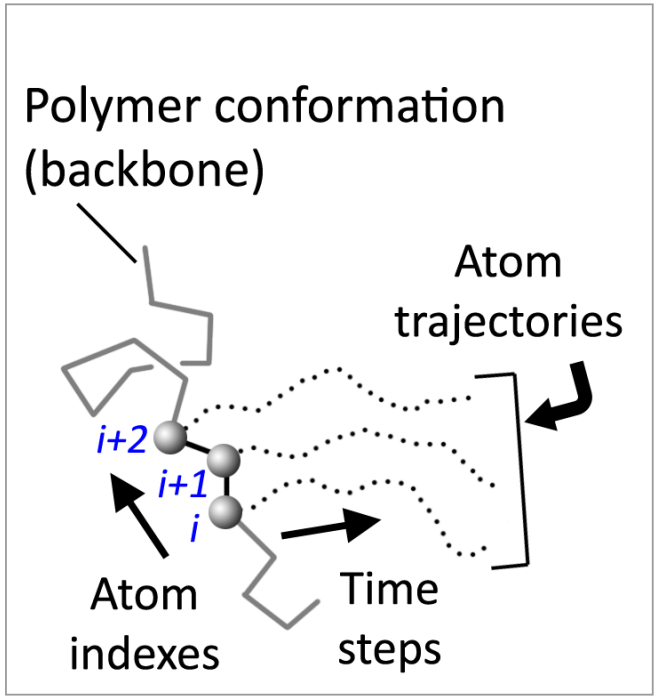
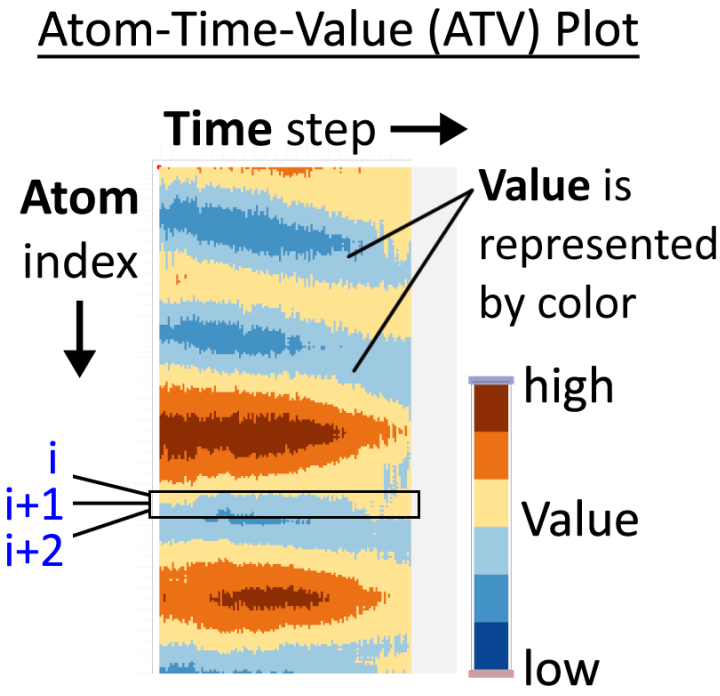
# Connect to Properties: Atom-Time-Value (ATV) Plots




Plot a local scalar attribute for each atom at every time step




## Examples of "values" or measures:

- Distance of backbone atoms from some origin (such as center of mass)
- Instantaneous velocities of backbone atoms
- Relative displacements of backbone atoms with respect to an initial set of locations (pseudo persistence length)

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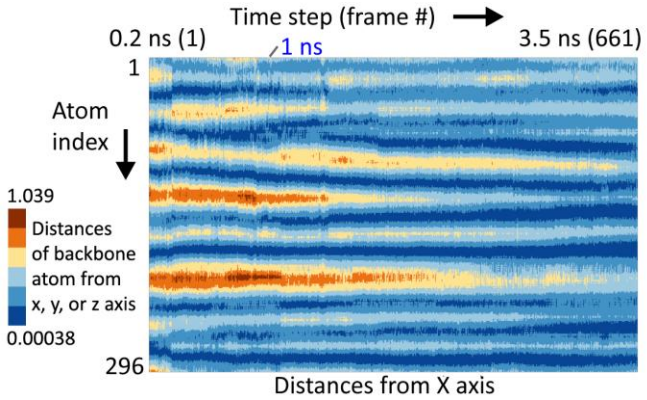
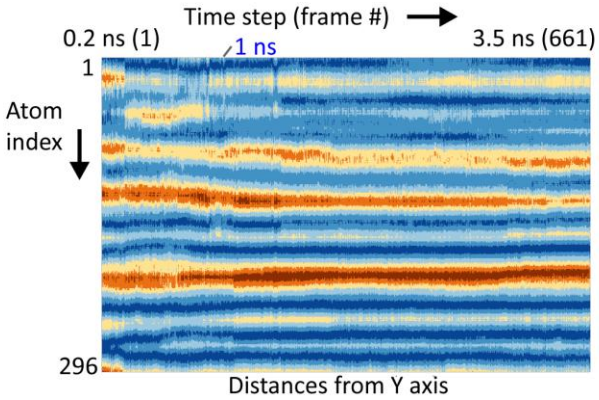
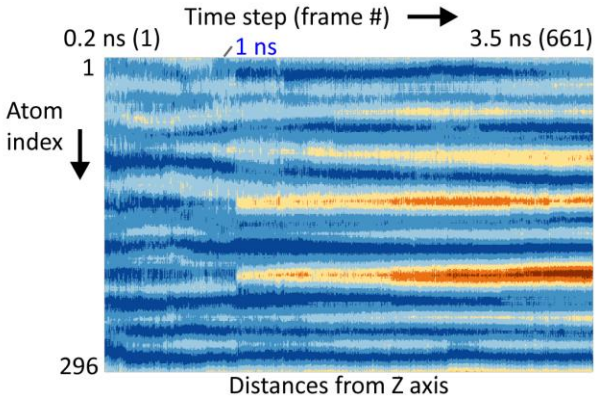
# APPLICATION: ATV Plots for Polymer-CNT Interactions

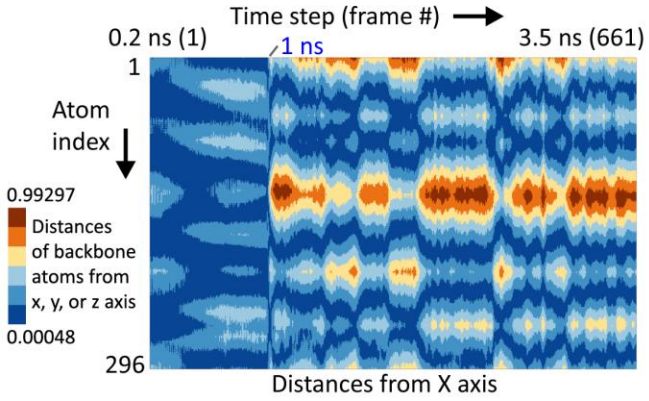
## Without Carbon Nanotube:

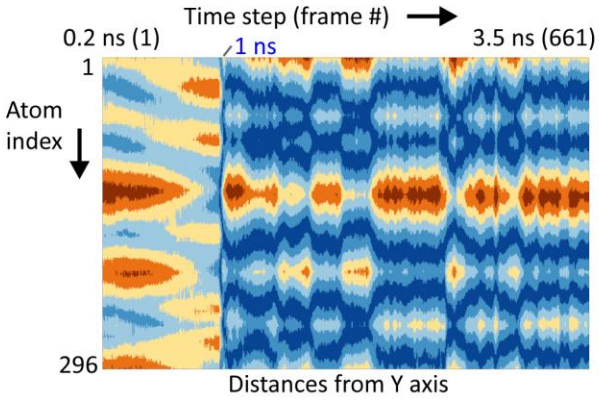


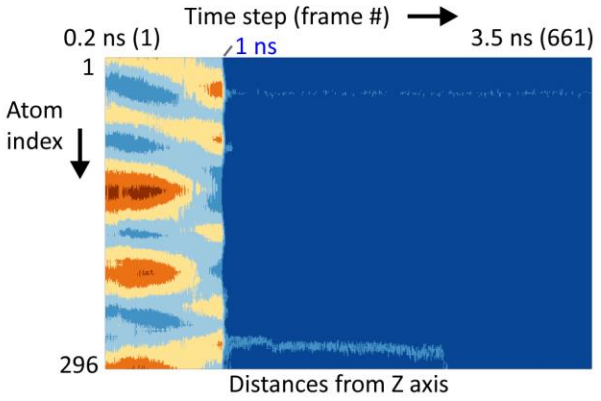



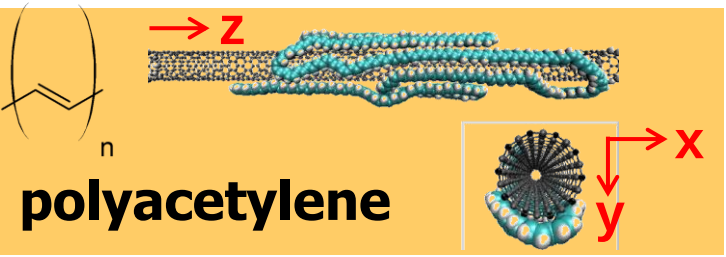




## With Carbon Nanotube:

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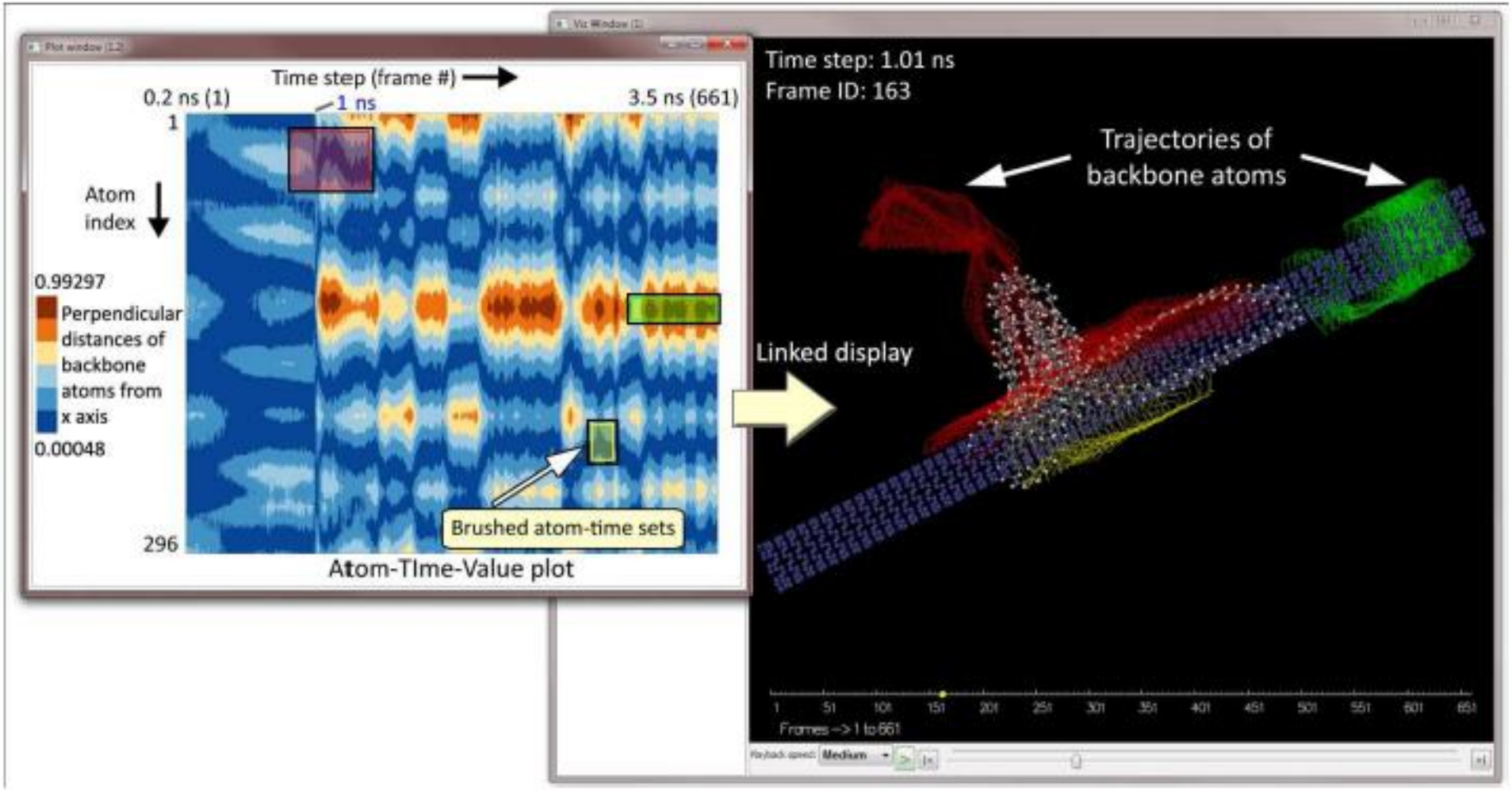
# Other Visualization Aspects: Linking and Brushing

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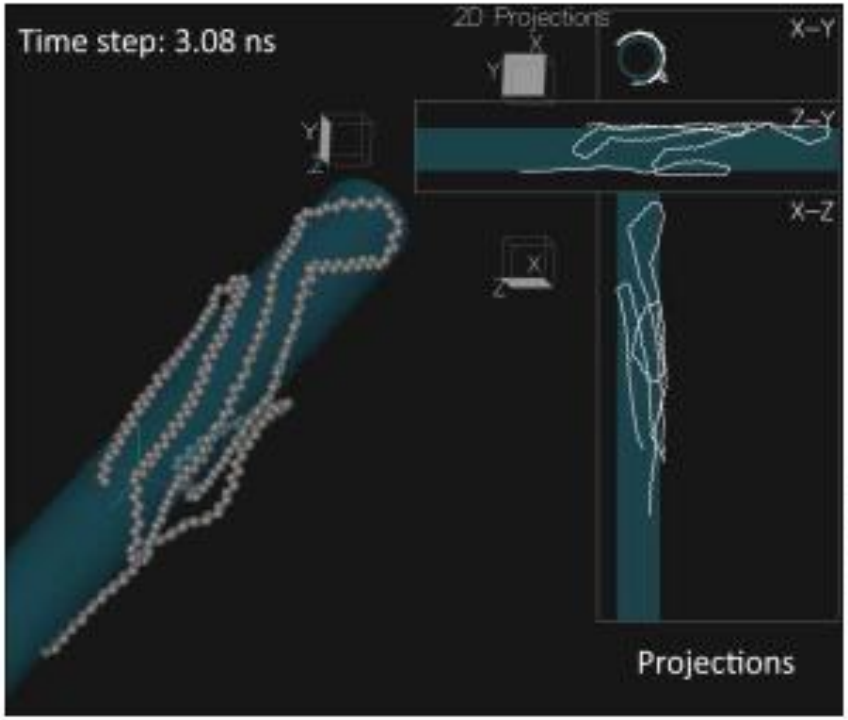
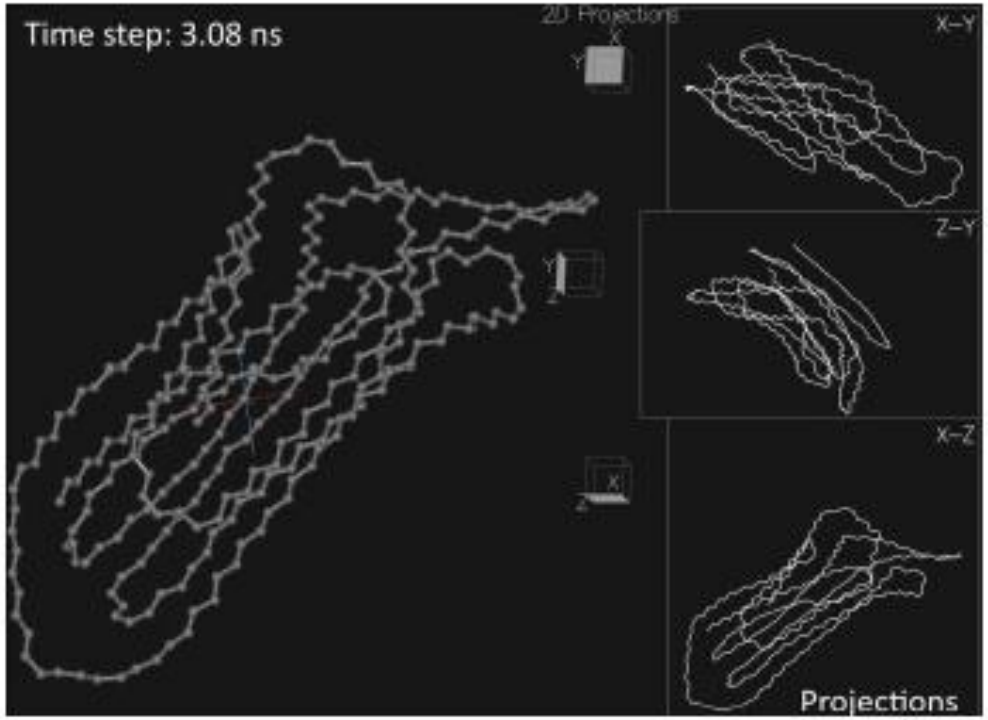
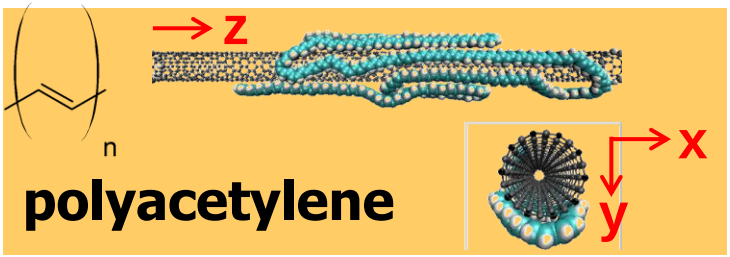
# Other Visualization Aspects: Projections

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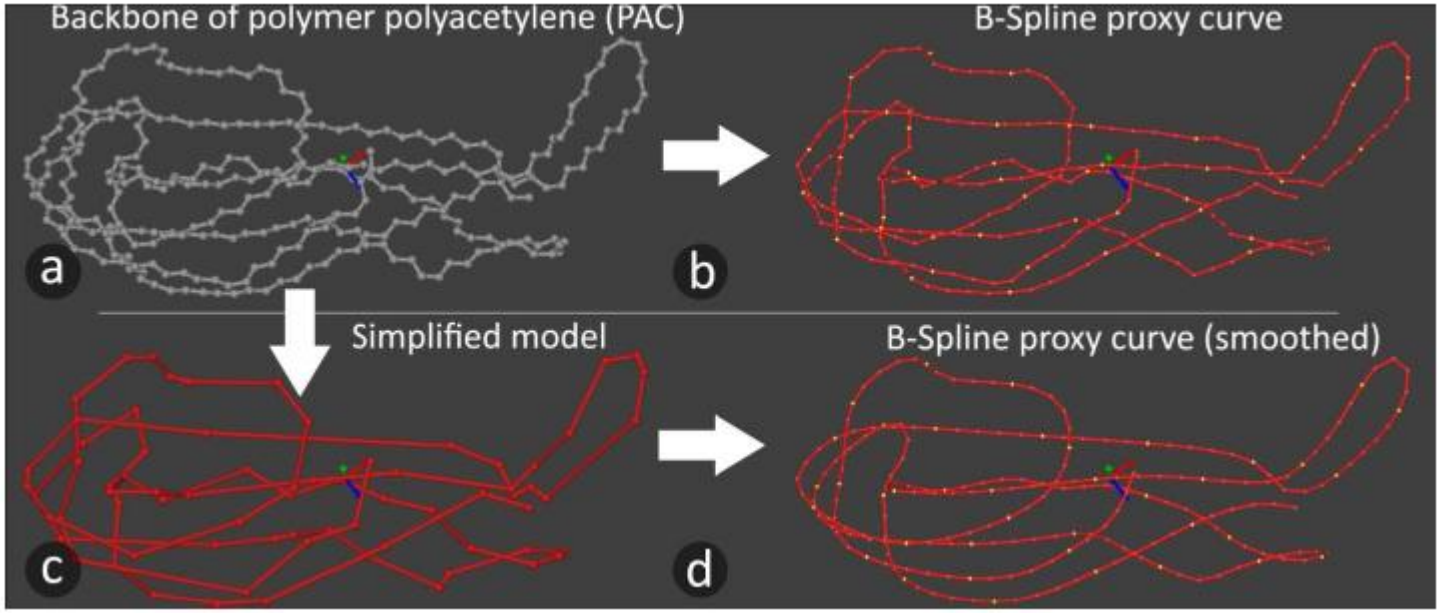
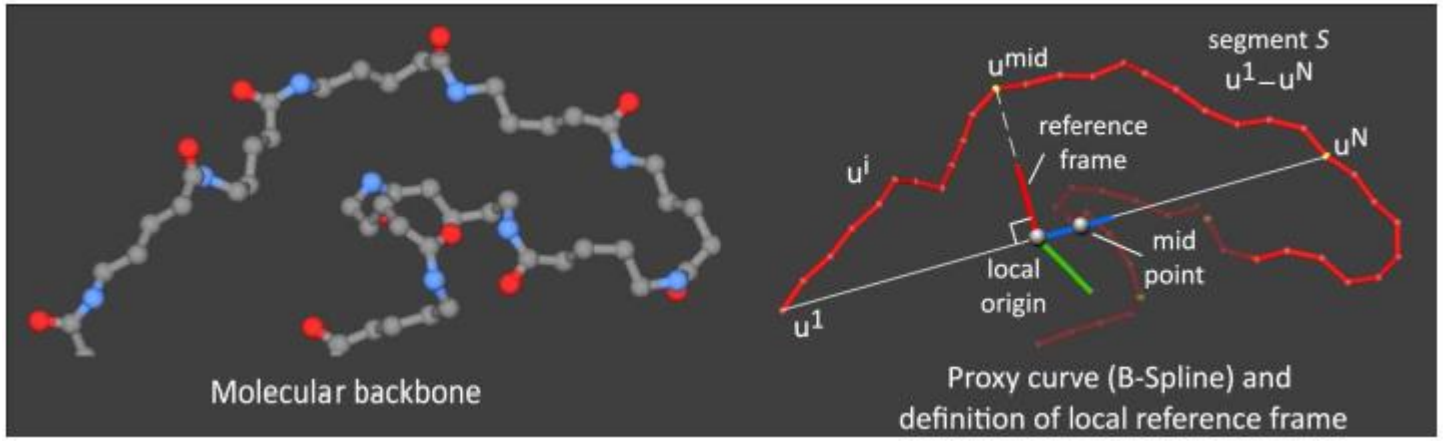
# Pattern Matching in Spatial and Temporal Dimensions

**Need to simplify the molecular (particle) structure in spatial dimensions**

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# Substructure Matching

- **Algorithm:**
  - Divide arc length curve into multiple segments
    - Segment size set by user
  - Compared with RMS Error between feature vectors
    - Tolerance controlled by user
  - Performed for all possible unique pairs of curve segments
- **Output:**
  - ID most commonly occurring features within polymer conformations among set of related polymers
    - Series of nylons
  - Explore spatial and temporal distributions of specific features
    - Start of crystal formation
  - Compare global structures of related polymers or under different scenarios
    - With/without a nanoparticle present

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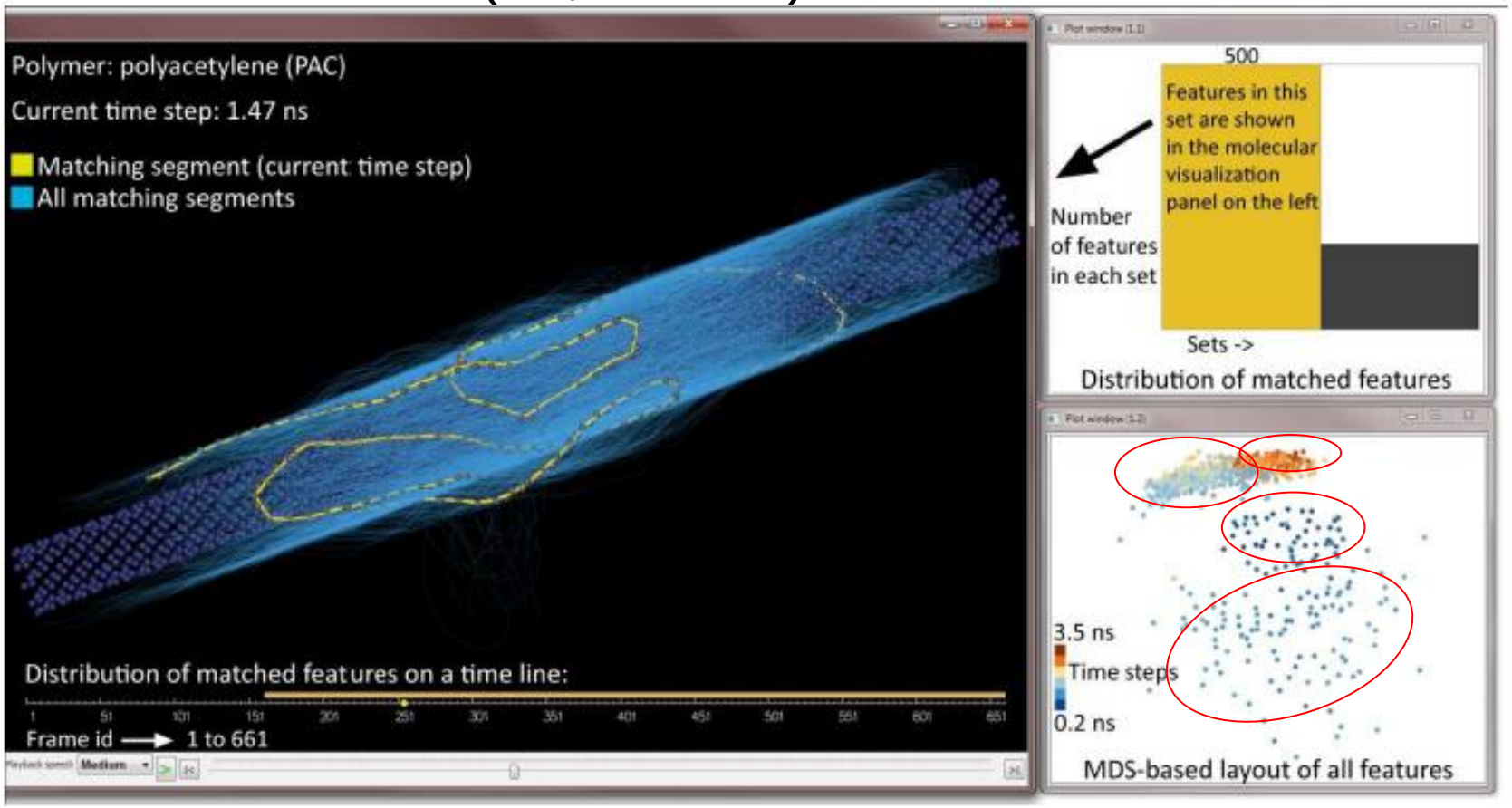
# Other Visualization Aspects: Clustering with MDS

**Multidimensional Scaling:**
High dimension ($\Re^N$) to
low dimension ($\Re^d$, d << N)

$$\text{Stress} = \sqrt{\sum_{i \neq j = 1}^{N} \left(D_{ij} - \|\mathbf{x}_i - \mathbf{x}_j\|\right)^2}$$

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# Other Details

- Stand-alone program
- Works with LAMMPS MD data sets
  - Will be tested on DPD soon
- Currently being extended to multi-molecule systems (polymer melts, solvent systems, etc.)
- Will be publicly available once multi-molecules are working (hopefully by end of the year)
  - On my website: www.te.ncsu.edu/mpasquinelli
  - On RENCI's website: www.renci.org
  - On LAMMPS website

# Contact Information


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(Yahoo, AIM, Google, MSN)

Phone:(919) 515.9426

**http://www.te.ncsu.edu/mpasquinelli**



**Funding:**

*Free software*
*(VMD, LAMMPS, PackMol)*

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RESEARCH ENGAGEMENT INNOVATION

**NC-ACS**
**Project**
**SEED**

NC STATE