CHARACTERIZING SELF ASSEMBLED MONOLAYERS USING SCANNING TUNNELING MICROSCOPY

By Robert Conwell

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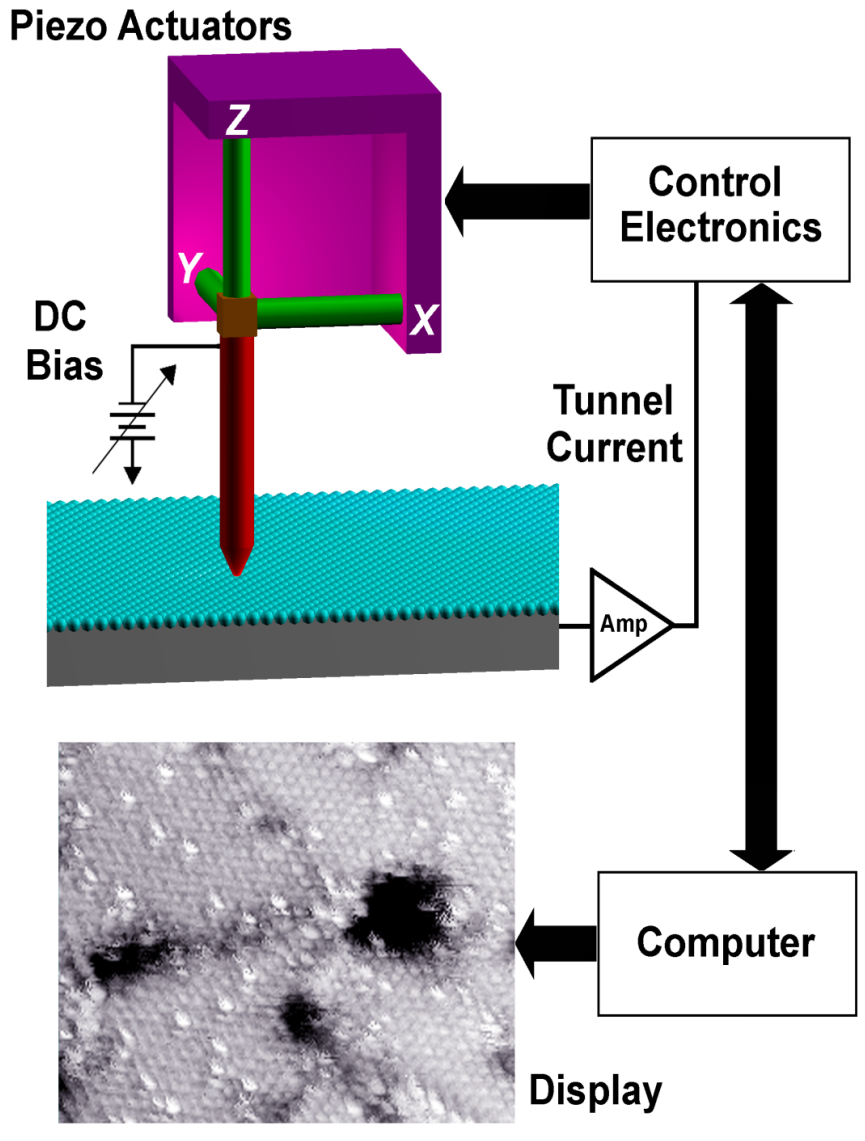
30 July 2019

SCANNING TUNNELING MICROSCOPE (STM) FUNDAMENTALS

- Electrons tunnel from atomically sharp tip to flat conductive sample

$$I \propto e^{-kd}$$

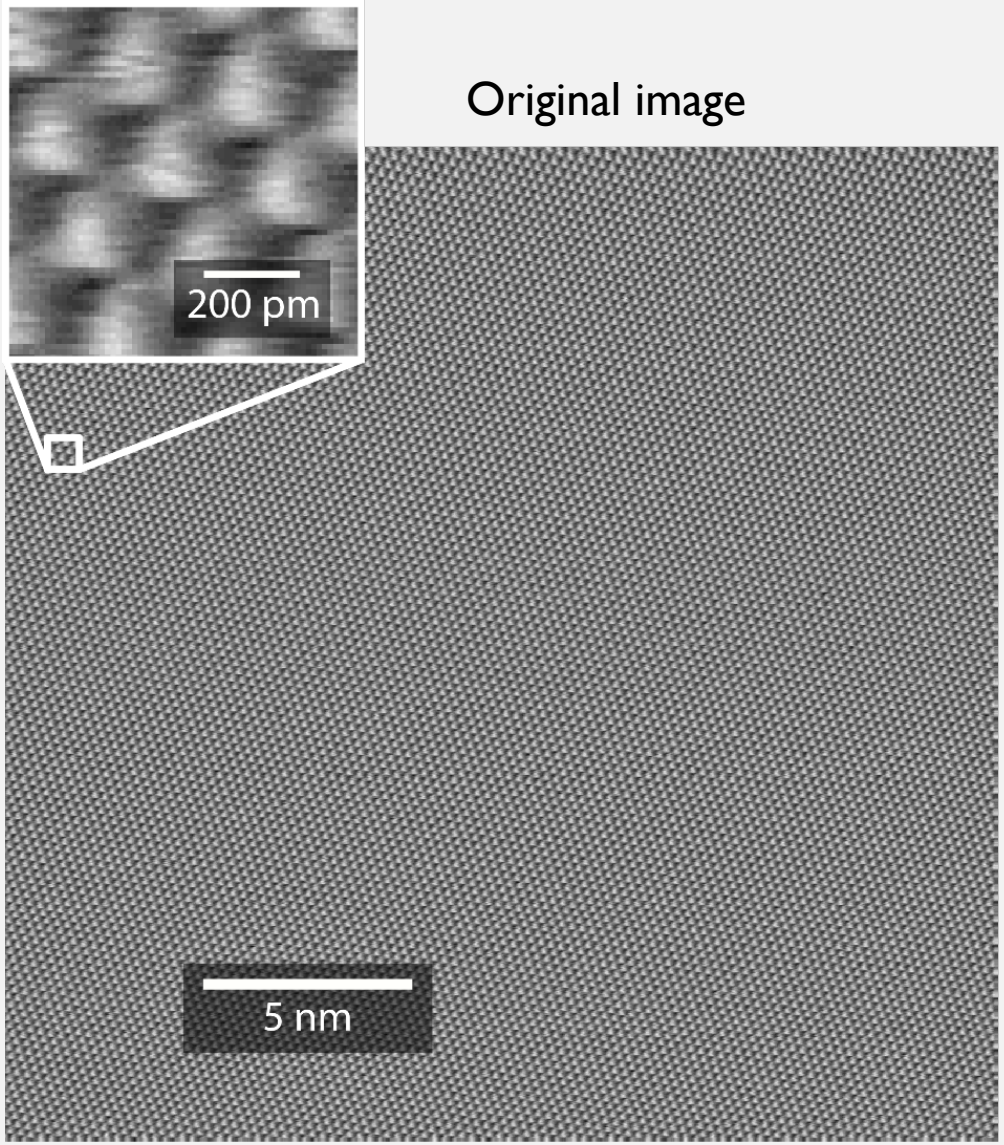
- Set point current and negative feedback for constant height
  - Low *I*: Tip too far, move forward
  - High *I*: Tip too close, move back
- Images surface topography for homogeneous samples



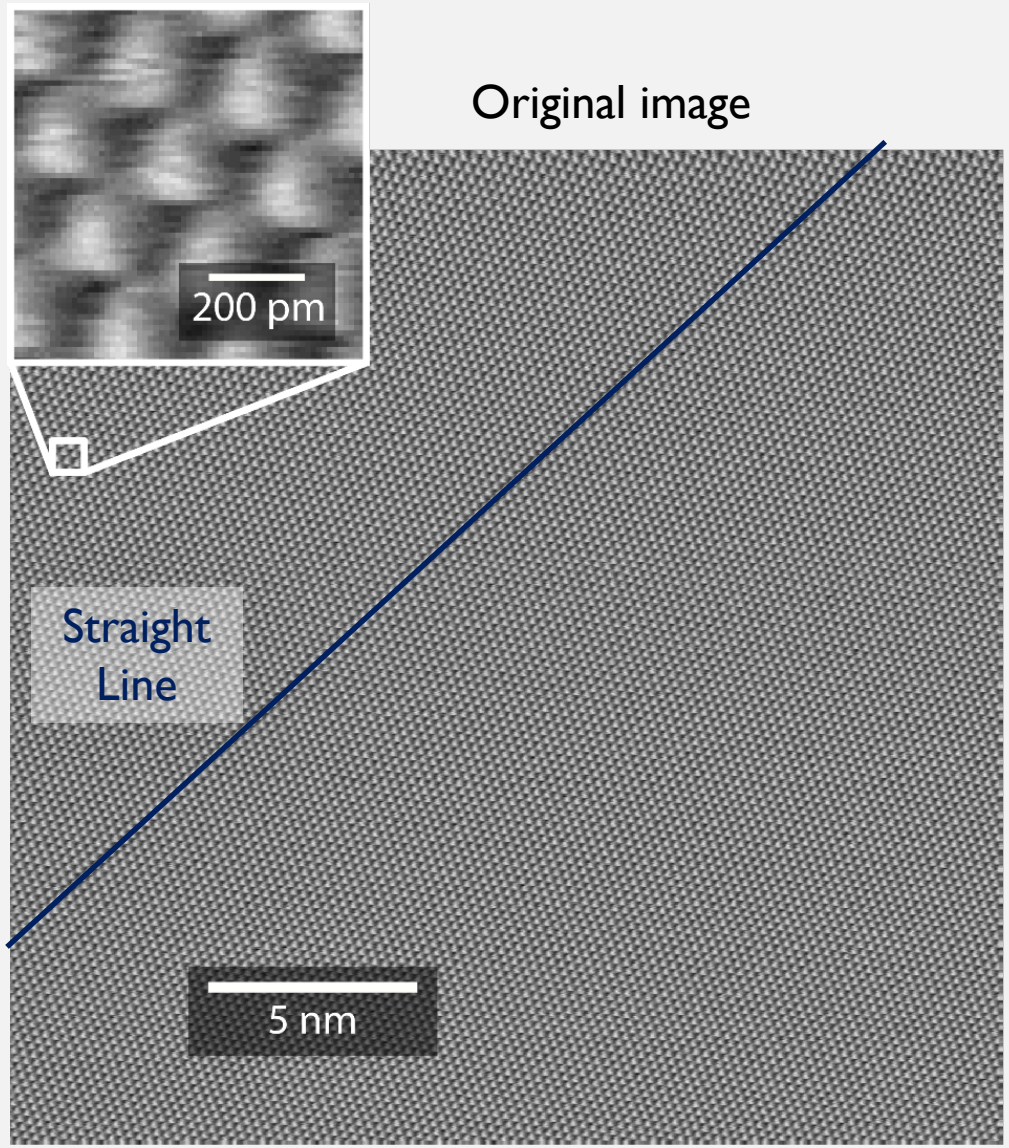
STM IMAGING EFFECTS

- Various imaging effects which distort the image
  - Drift
  - Hysteresis
  - Creep
- Either image is distorted or SAMs are not a lattice
  - Latter is highly unlikely
- Apply image correction in MATLAB

Original image



M.P.Yothers, A. E. Browder, and L. A. Bumm, *Rev. Sci. Instrum.* **88** (1), 013708 (2017).



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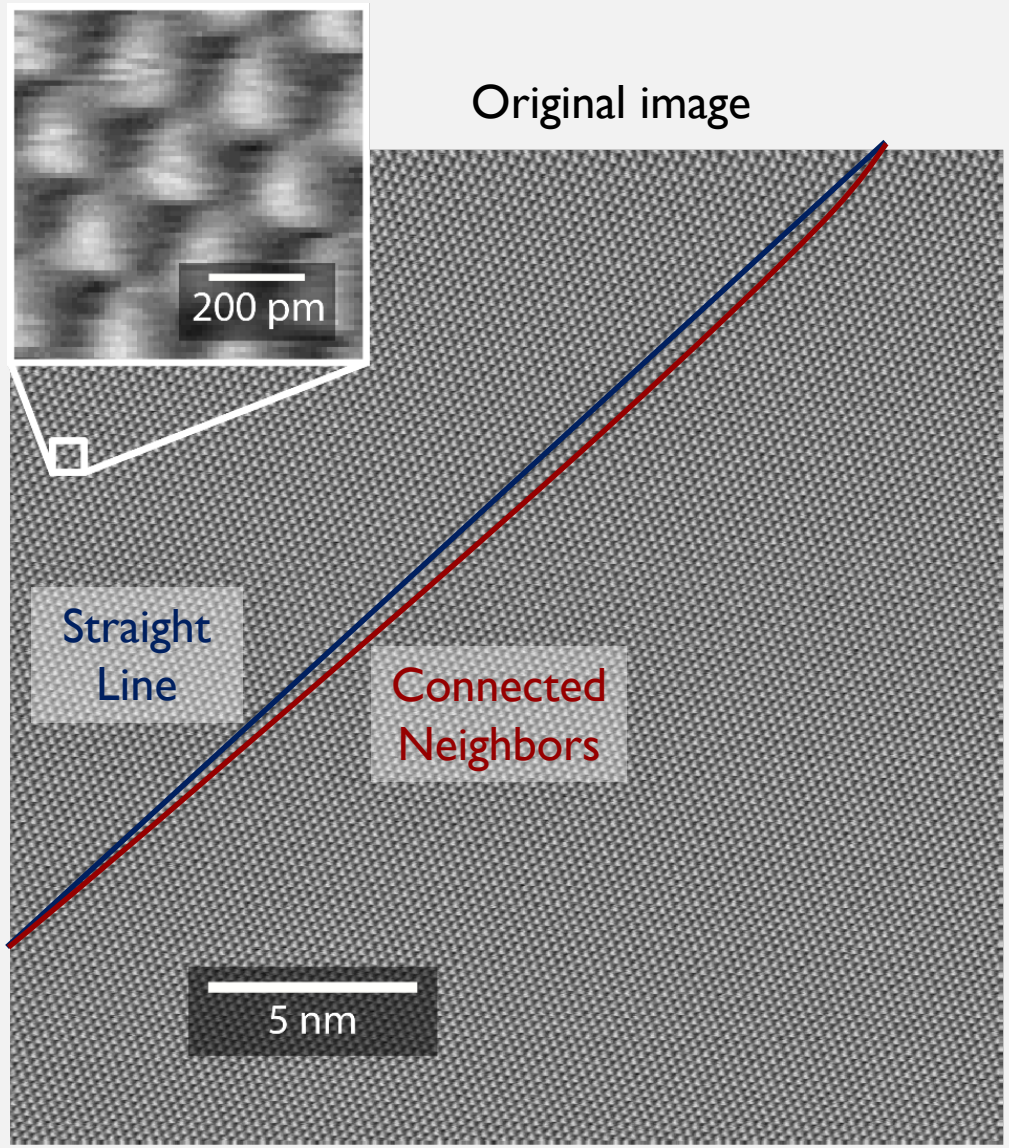

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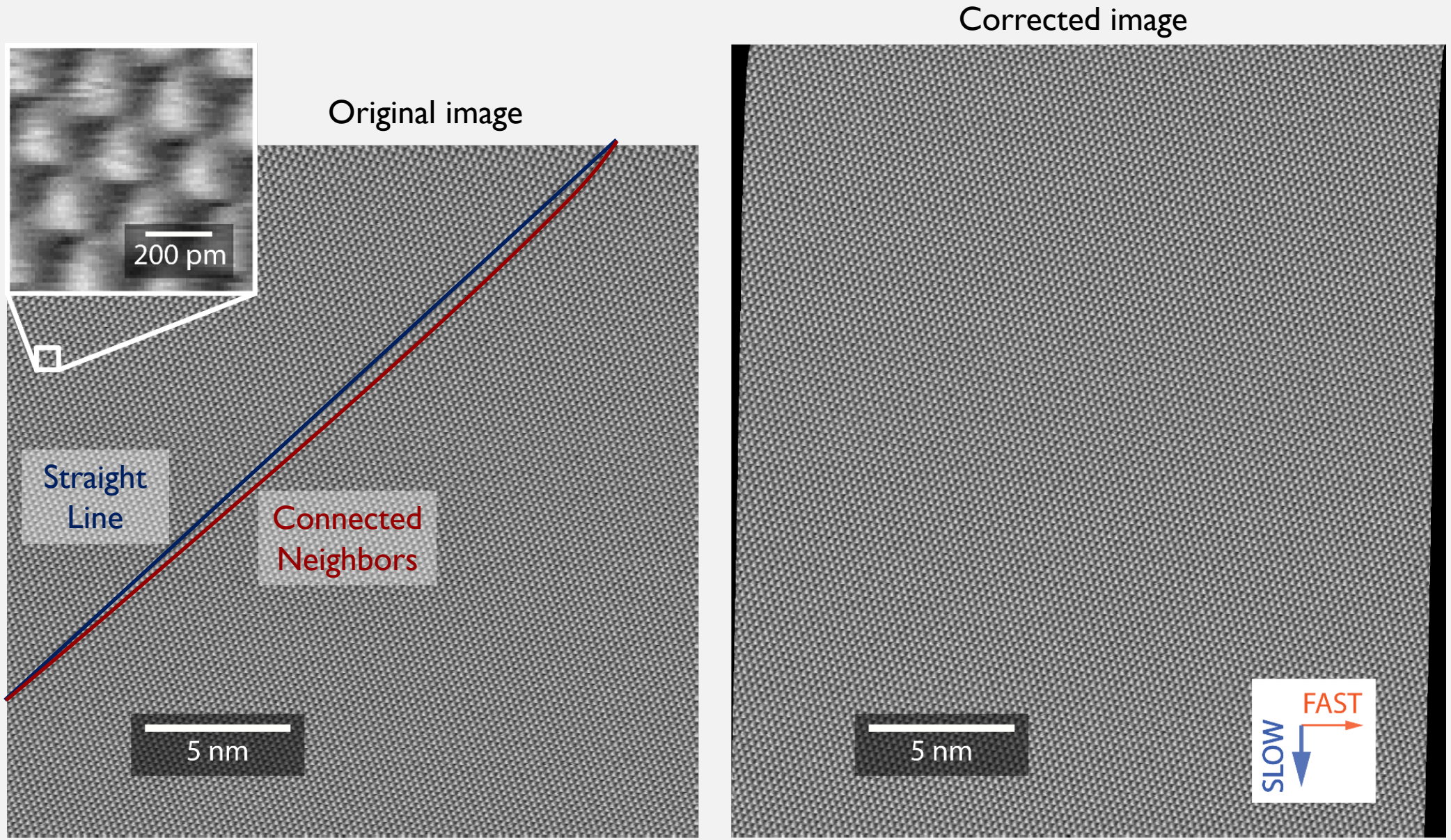

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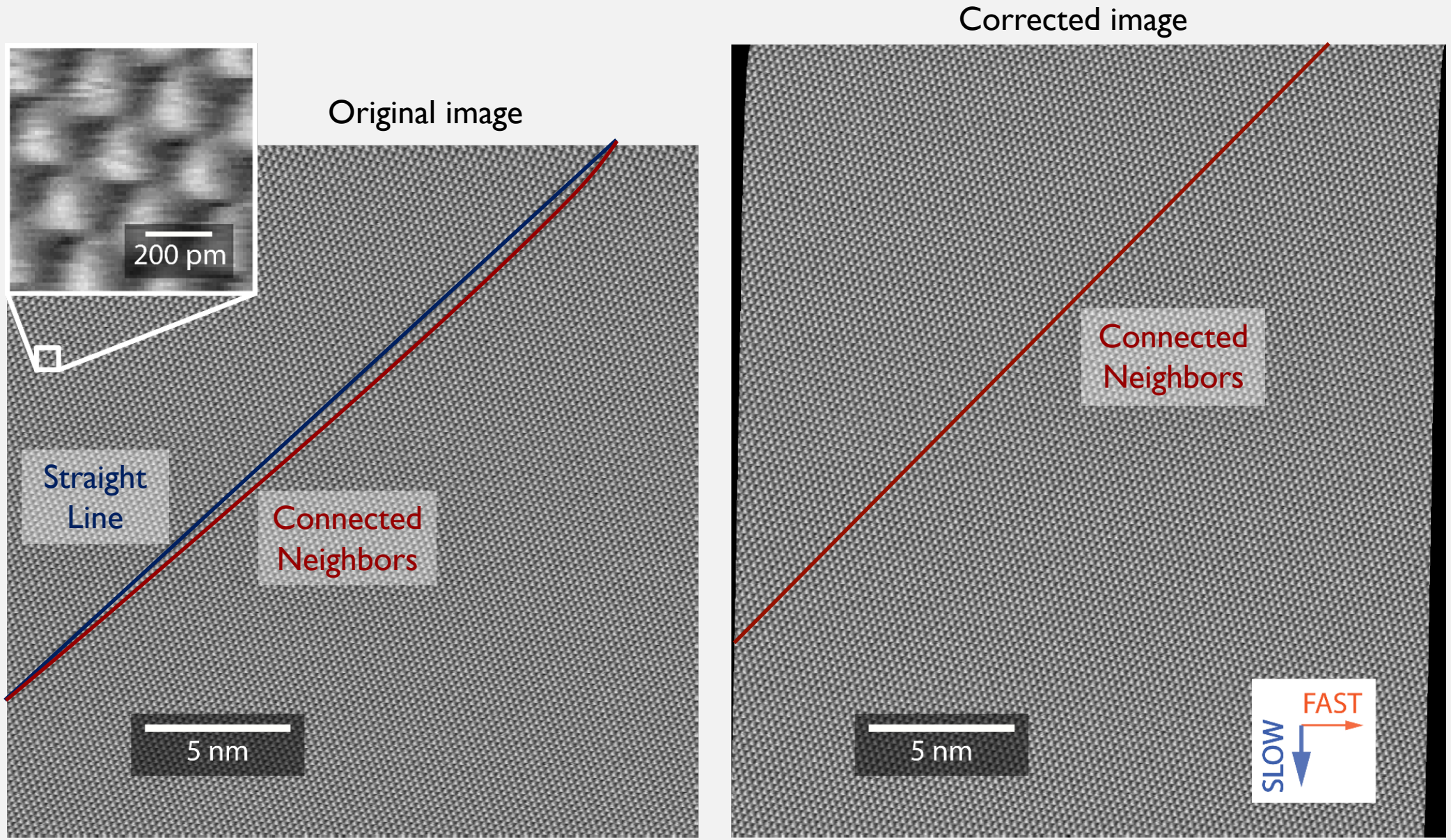

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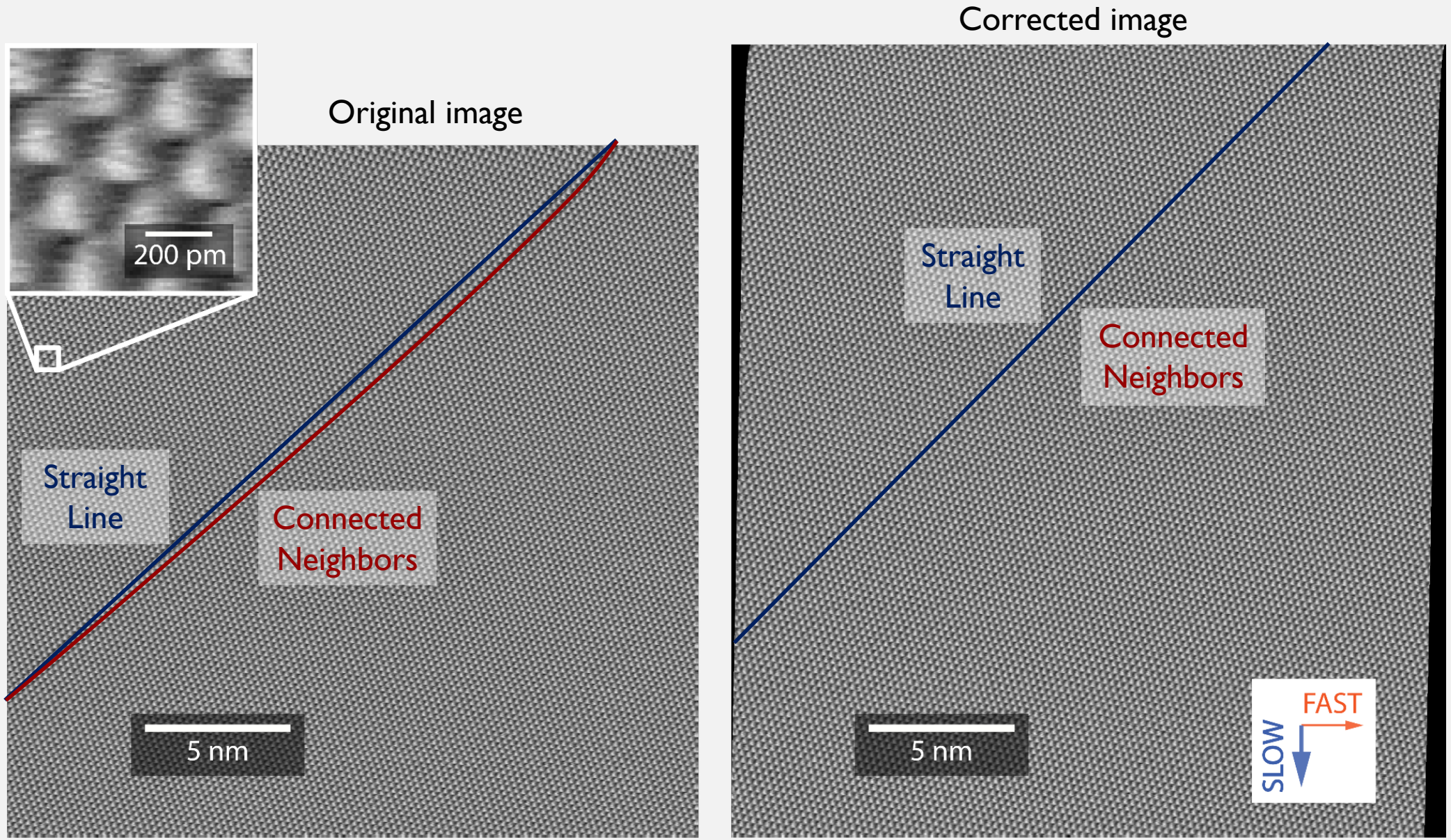

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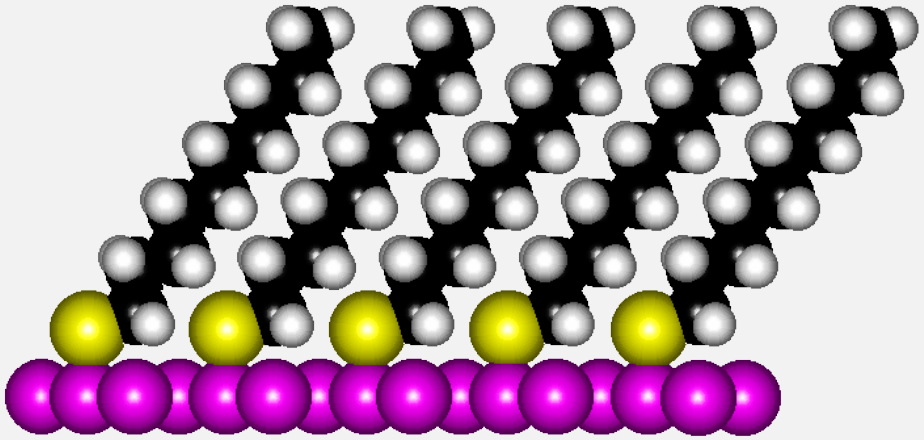
ALKANETHIOL SELF ASSEMBLED MONOLAYERS (SAMs)

- Alkanethiol – hydrocarbon chain with sulfur at the end
- Self assemble – spontaneously grow 2D crystal from alkanethiol vapor
- Monolayer – Only a molecule thick

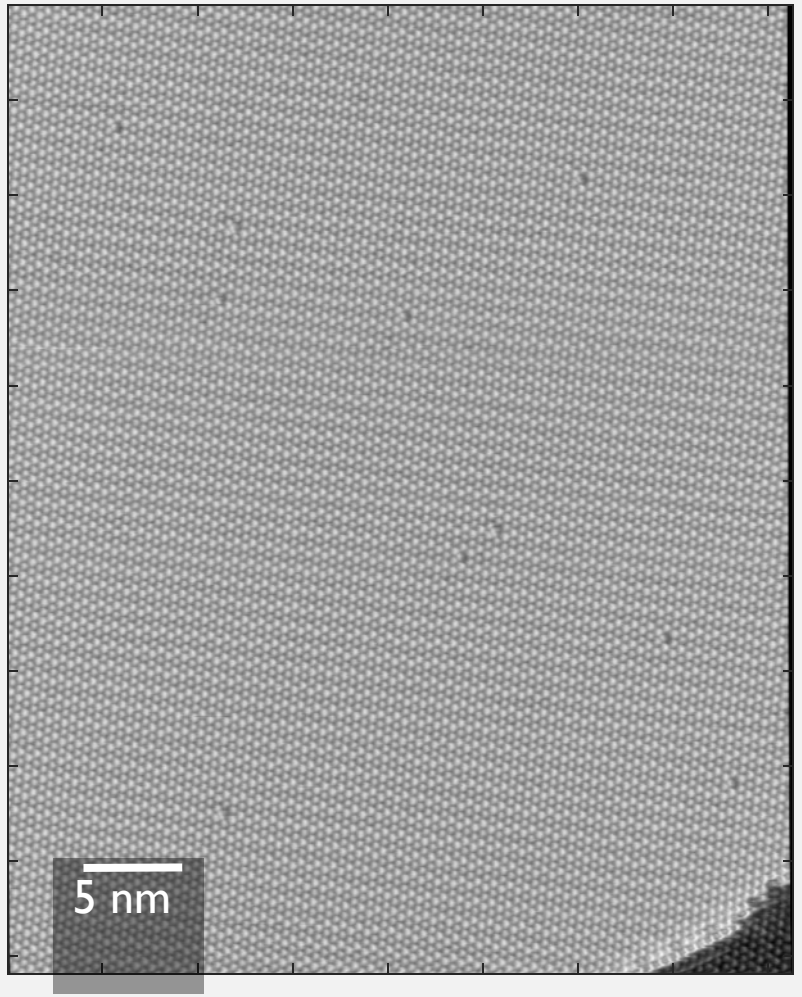


Decanethiol – C10

ALKANETHIOL SELF ASSEMBLED MONOLAYERS (SAMs)

- Alkanethiol SAMs on gold substrate
- Abbreviate name by length of hydrocarbon chain

Name	Abbreviation
Octanethiol	C8
Nonanethiol	C9
Decanethiol	C10
Undecanethiol	C11
Dodecanethiol	C12



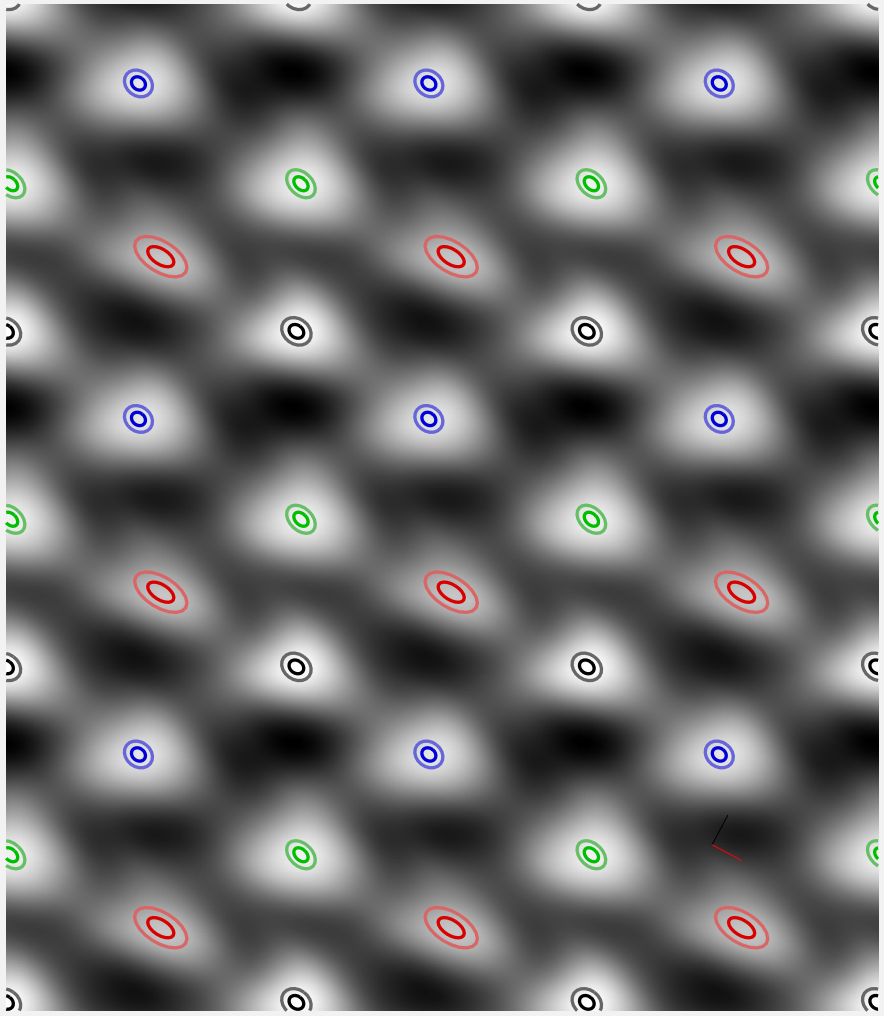
C10 Sample 2019 #3
2019_06_17_0033

CRYSTAL LATTICE

- Crystal – repeating arrangement of atoms
- Two components
  - Lattice → How to repeat
  - Basis → What is being repeated

- Unit cell → Unit cell is the smallest group of atoms which can be repeated to reconstruct the entire crystal, i.e. contains all information of the crystal

UNIT CELL & LOCATION CONFIDENCE



- Averaged unit cell image
  - Grayscale
- Ellipses - location confidence
  - Colored by basis site
  - Center – Mean location
  - Inner ellipse 1σ, outer 2σ

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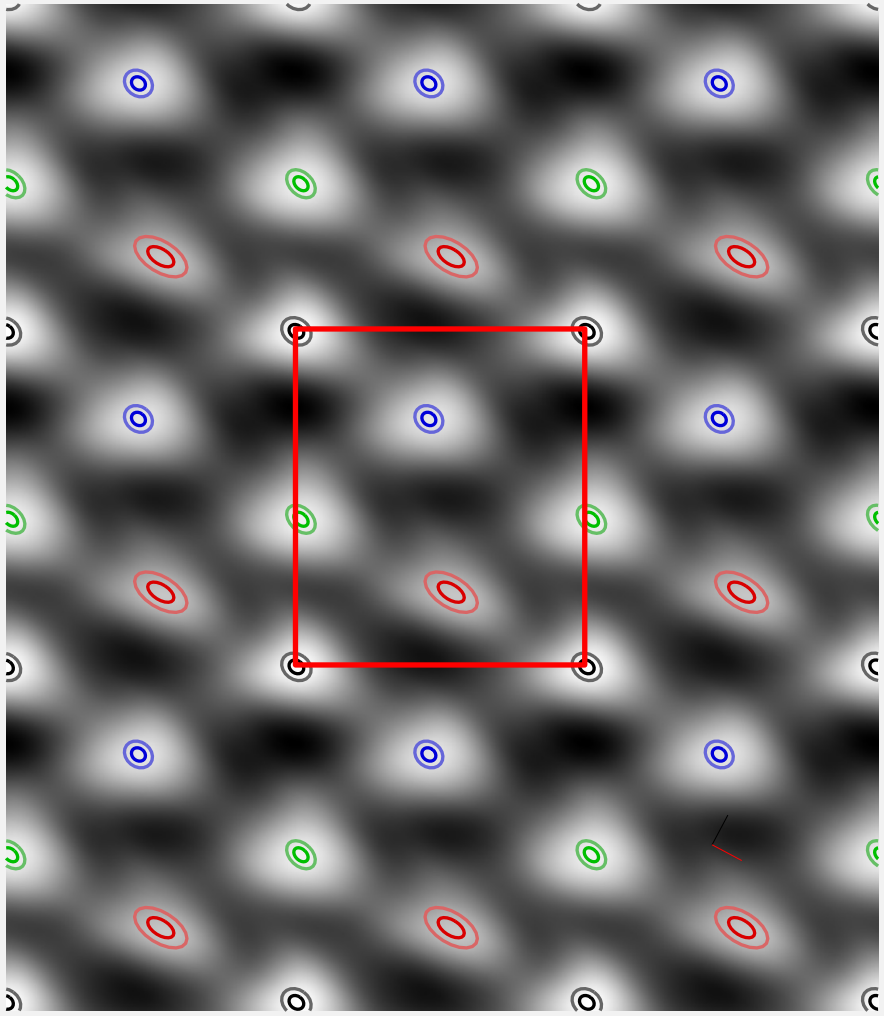

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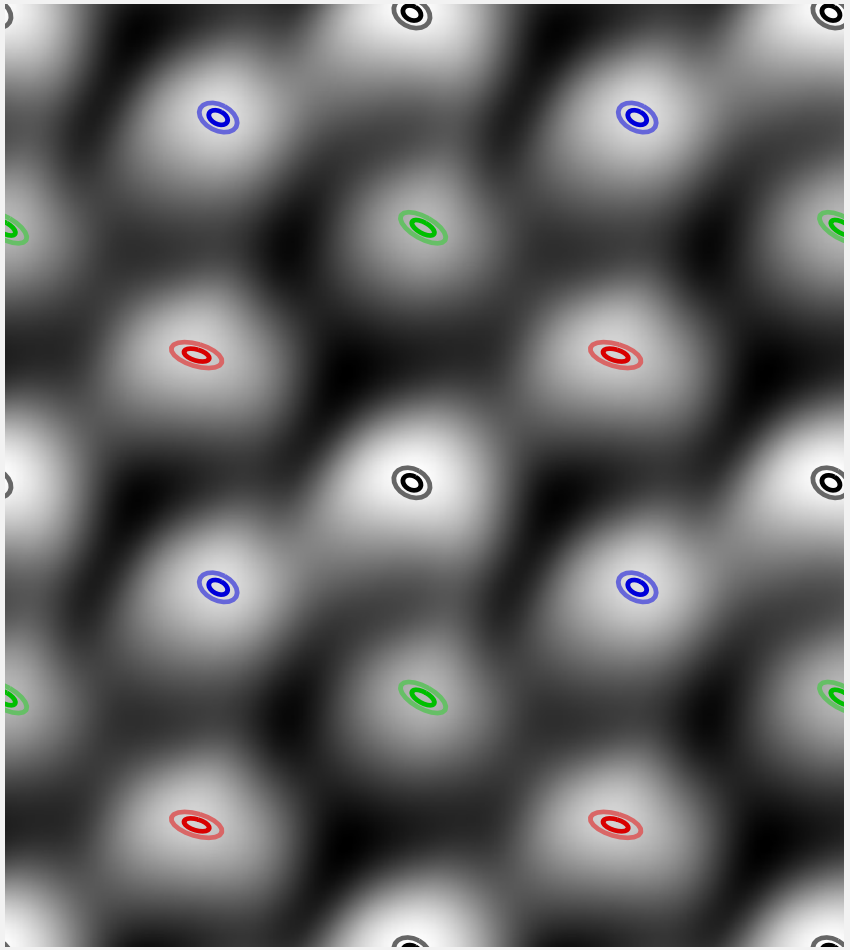
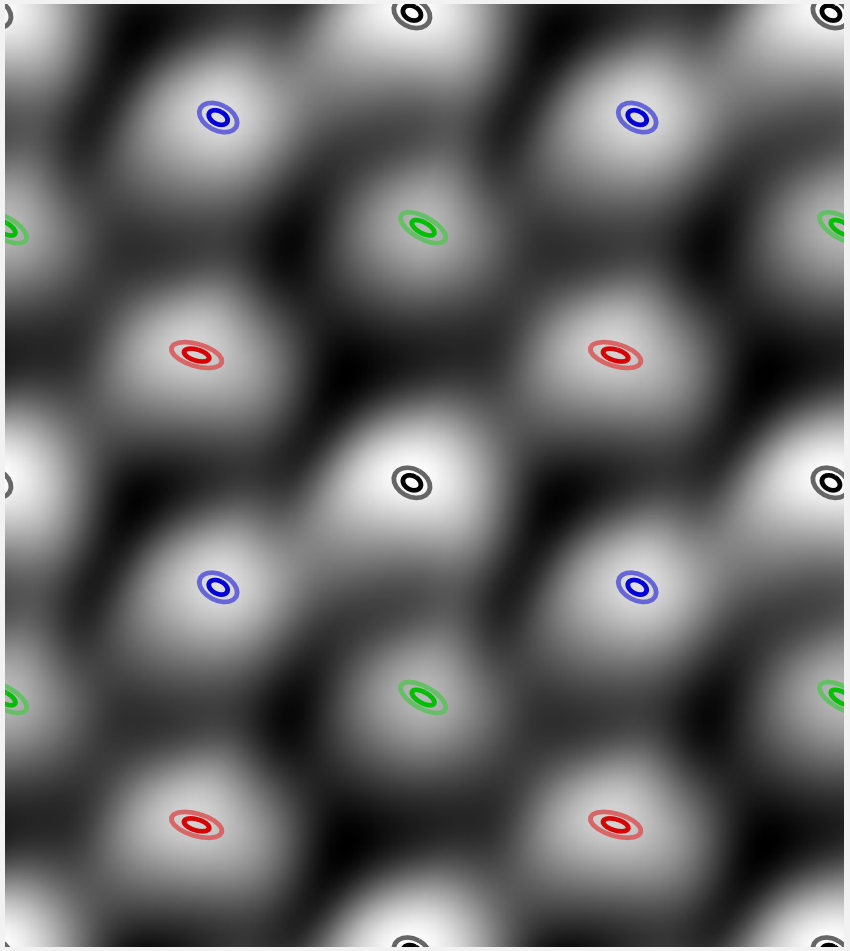
ALKANETHIOL CRYSTAL

- All 4 molecule colors are alkanethiol
- Structure is very similar to a one-molecule basis
- How do we compare these structures?



STRUCTURE FINGERPRINT

- Molecule ends are close to one-molecule basis lattice sites
- Fingerprint plot shows distance from these sites
- Easier to see differences between structures



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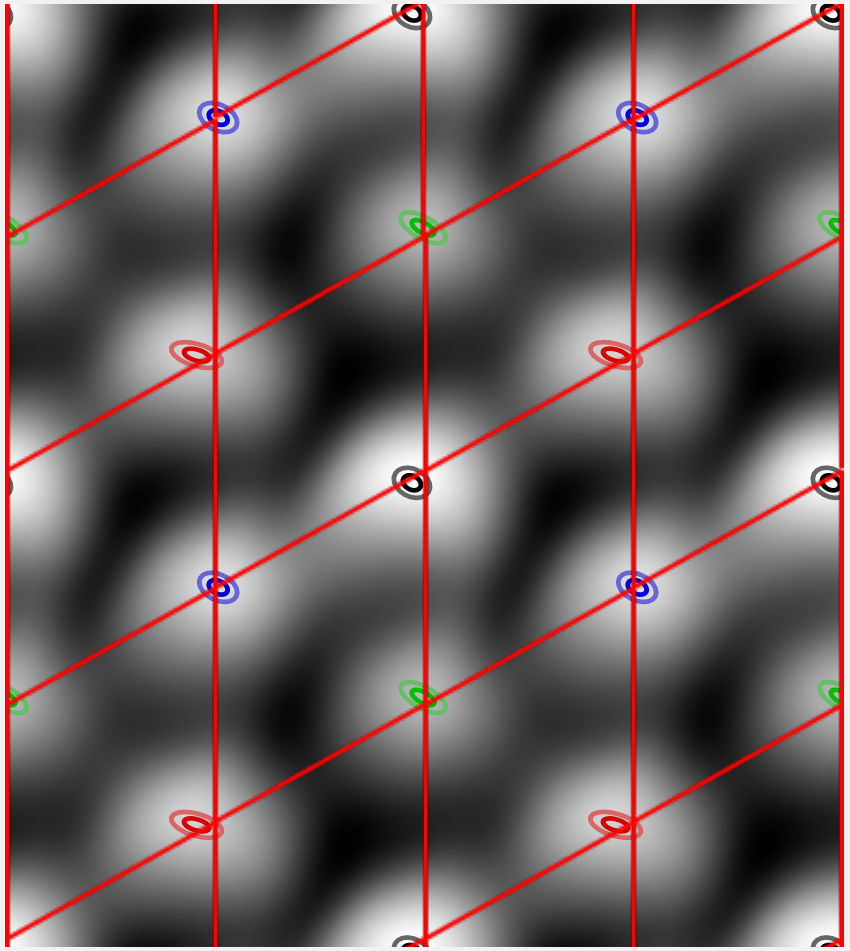

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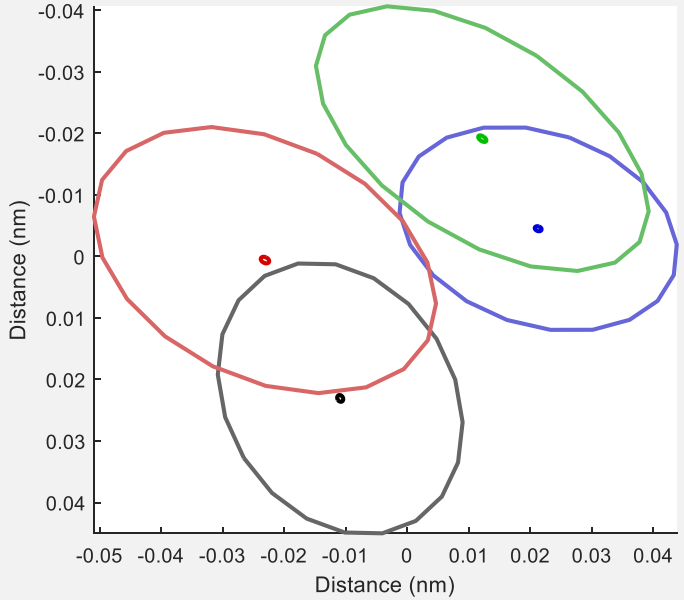

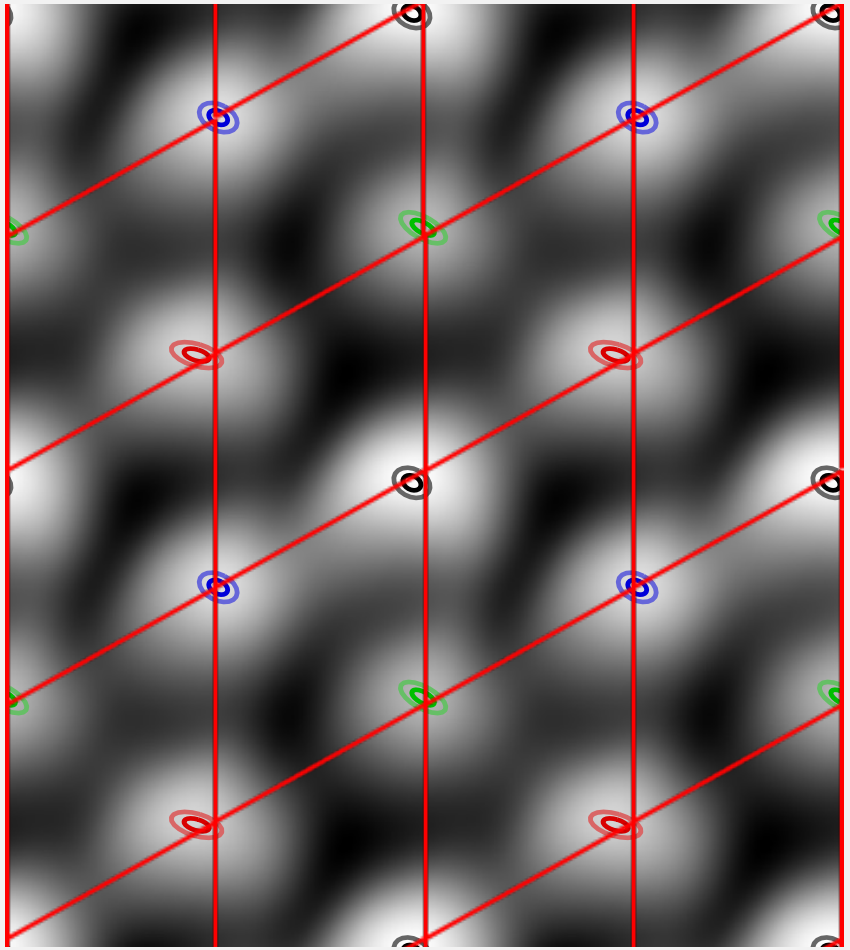

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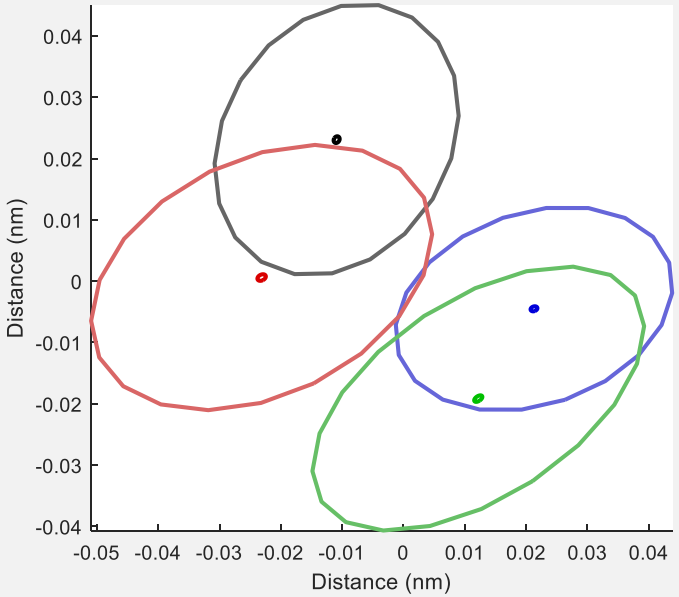

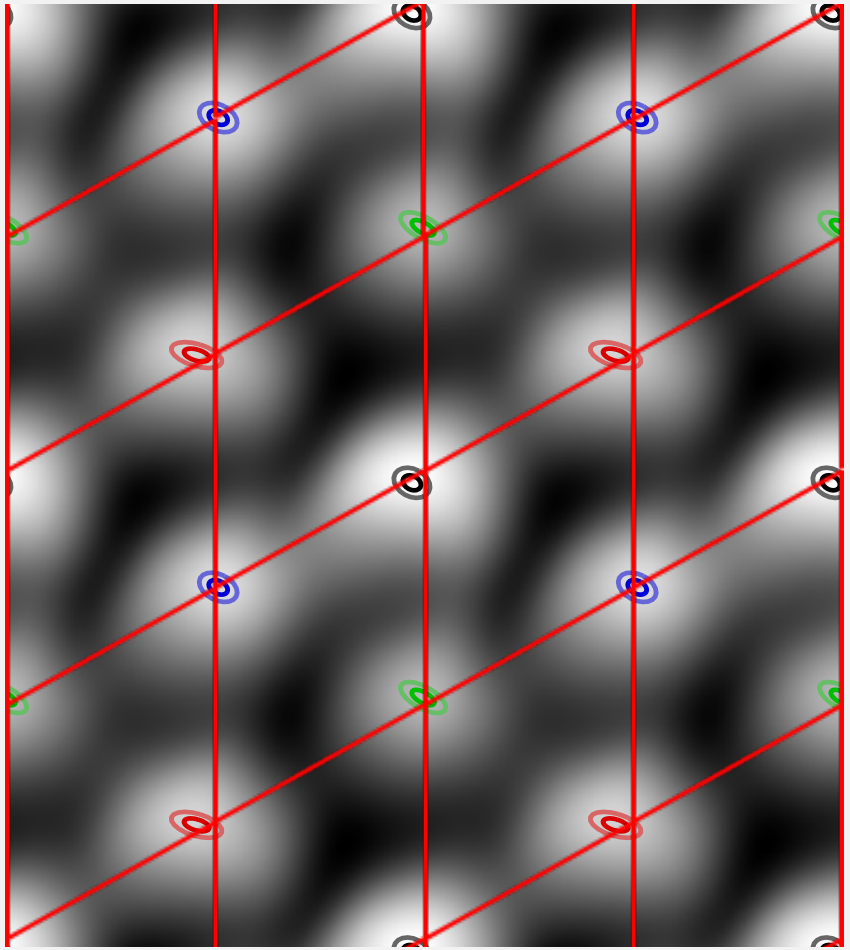

MOTIVATION

- **Does selecting molecules on/near a boundary skew results?**
  - Close to a boundary, the crystal may be strained
  - Analysis on boundary vs Analysis 5-10 molecules away from boundary

- Are chains of odd and even length structurally different?
  - Can we tell odd from even by looking at them?

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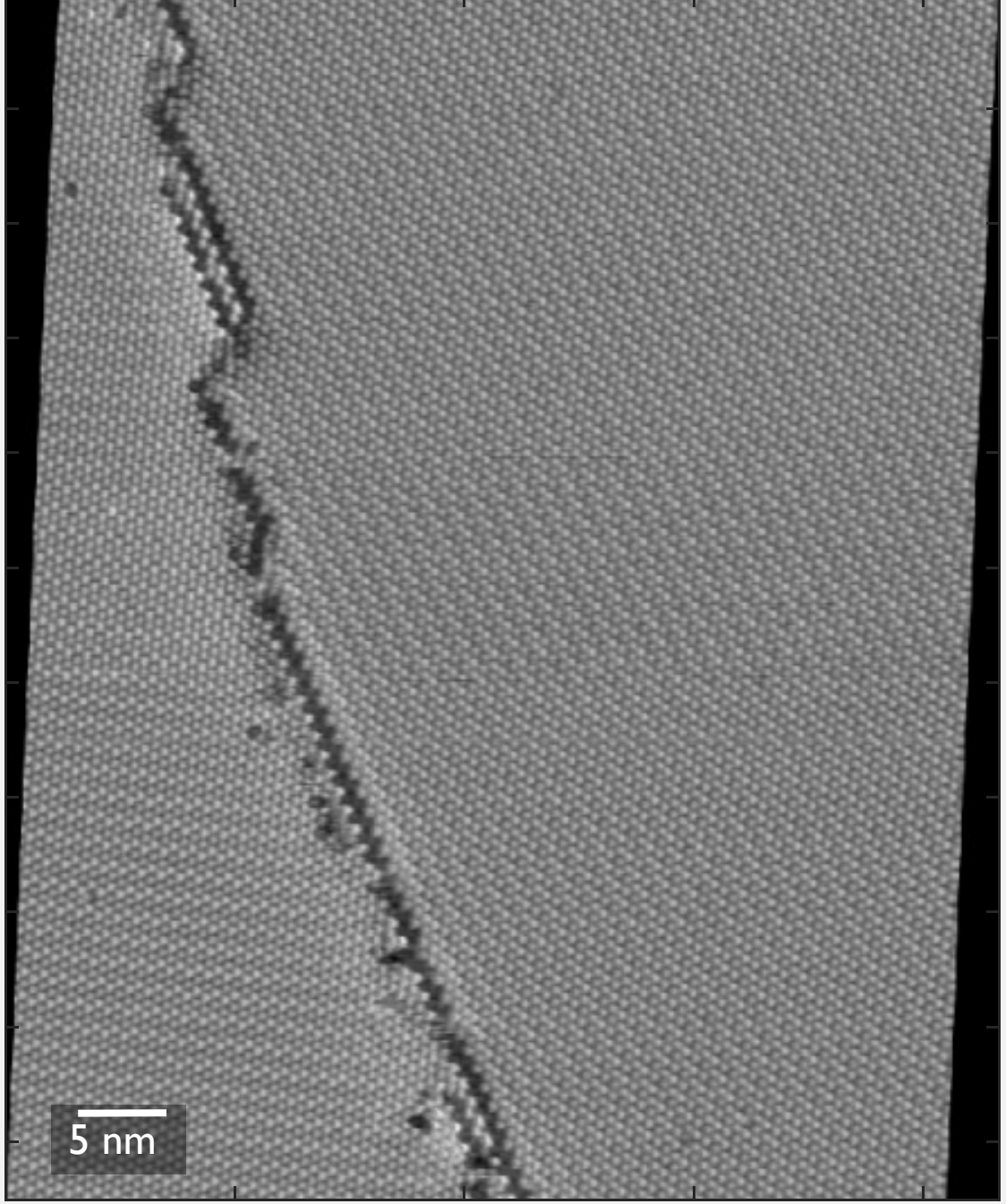
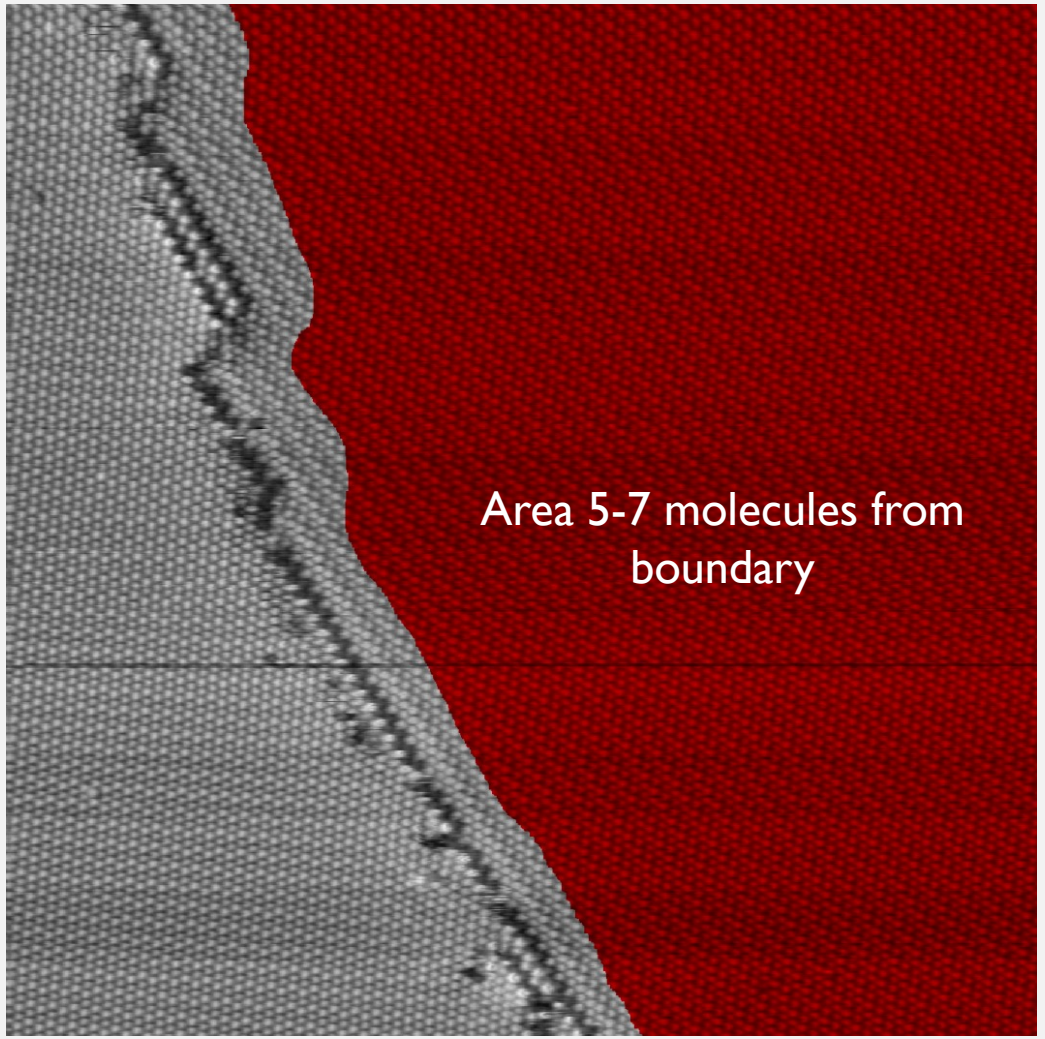
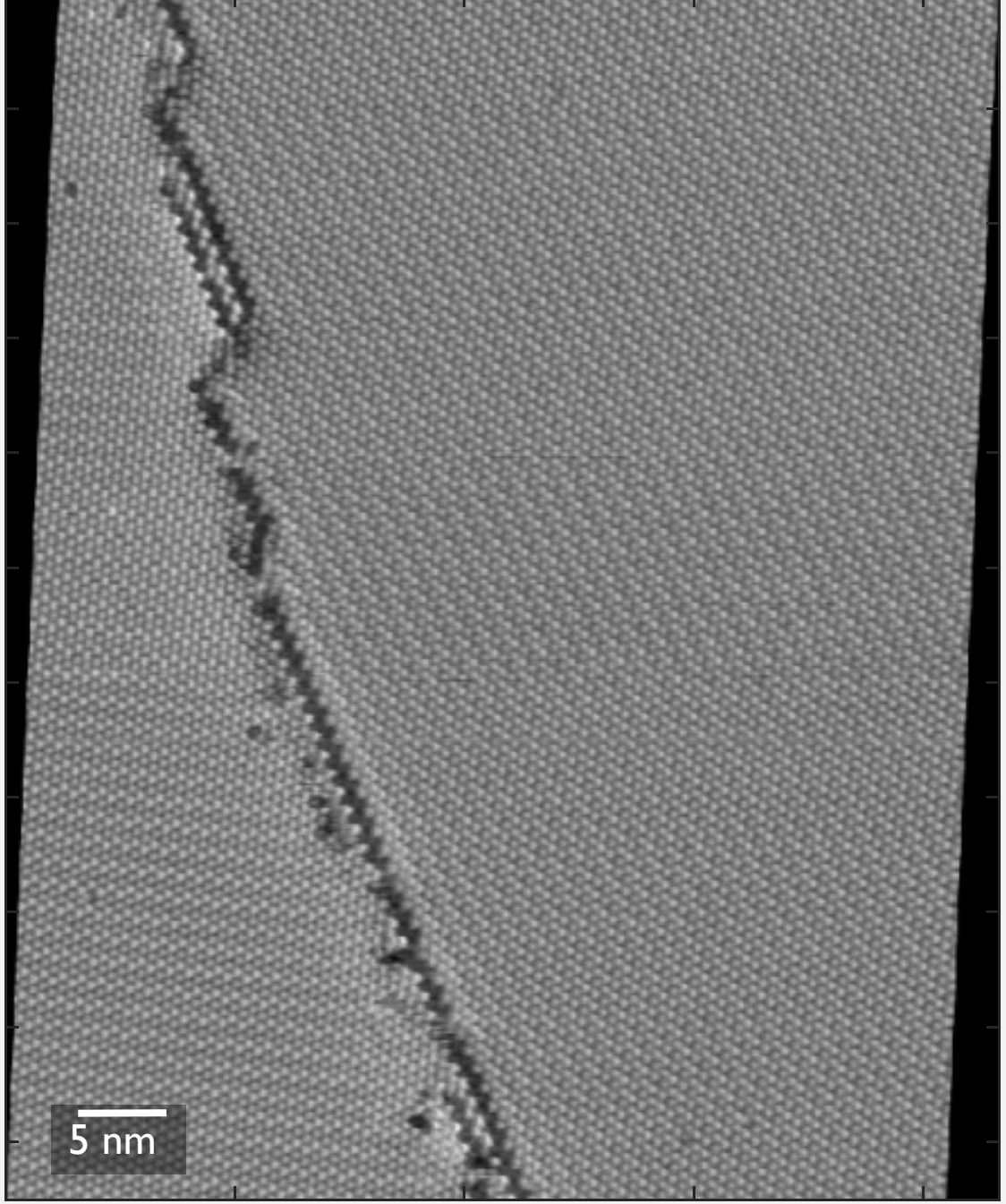
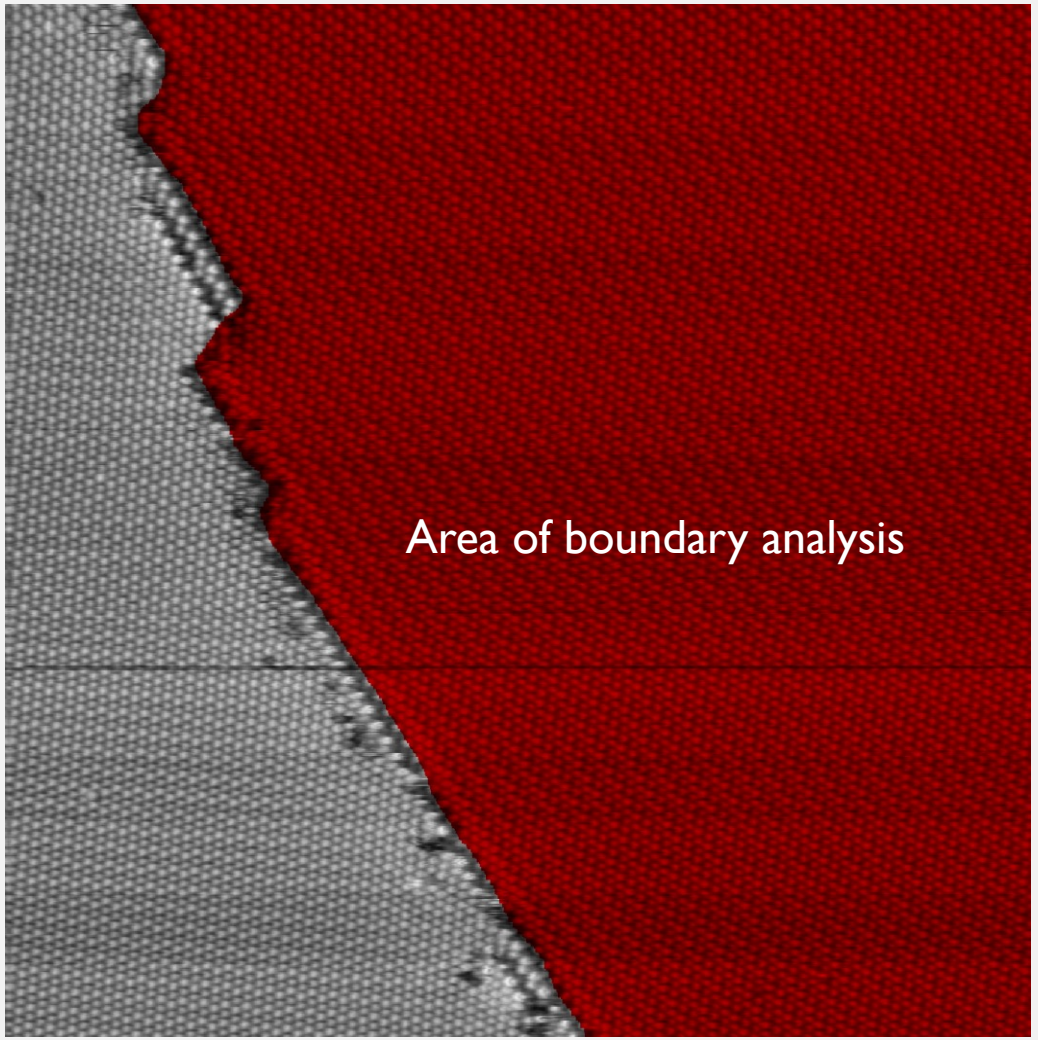




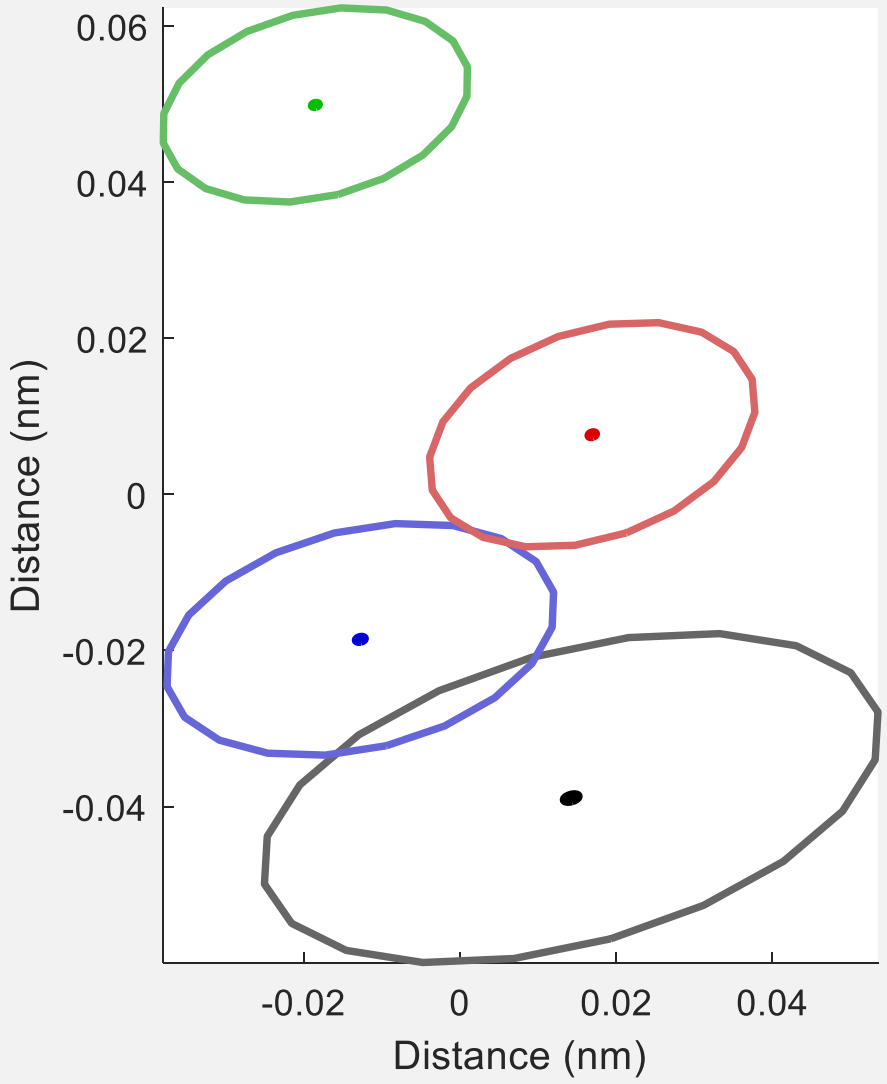
2019_06_17_0024 C10
(2019 #3)



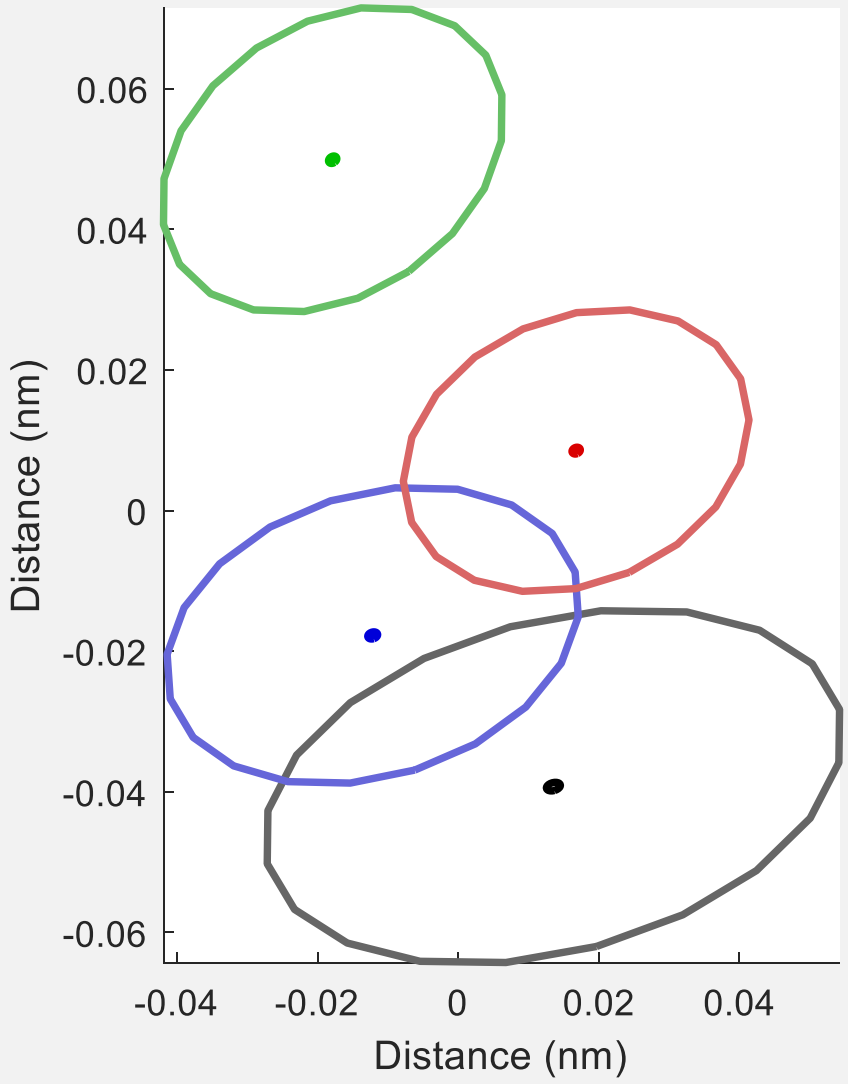


2019_06_17_0024 C10
(2019 #3)

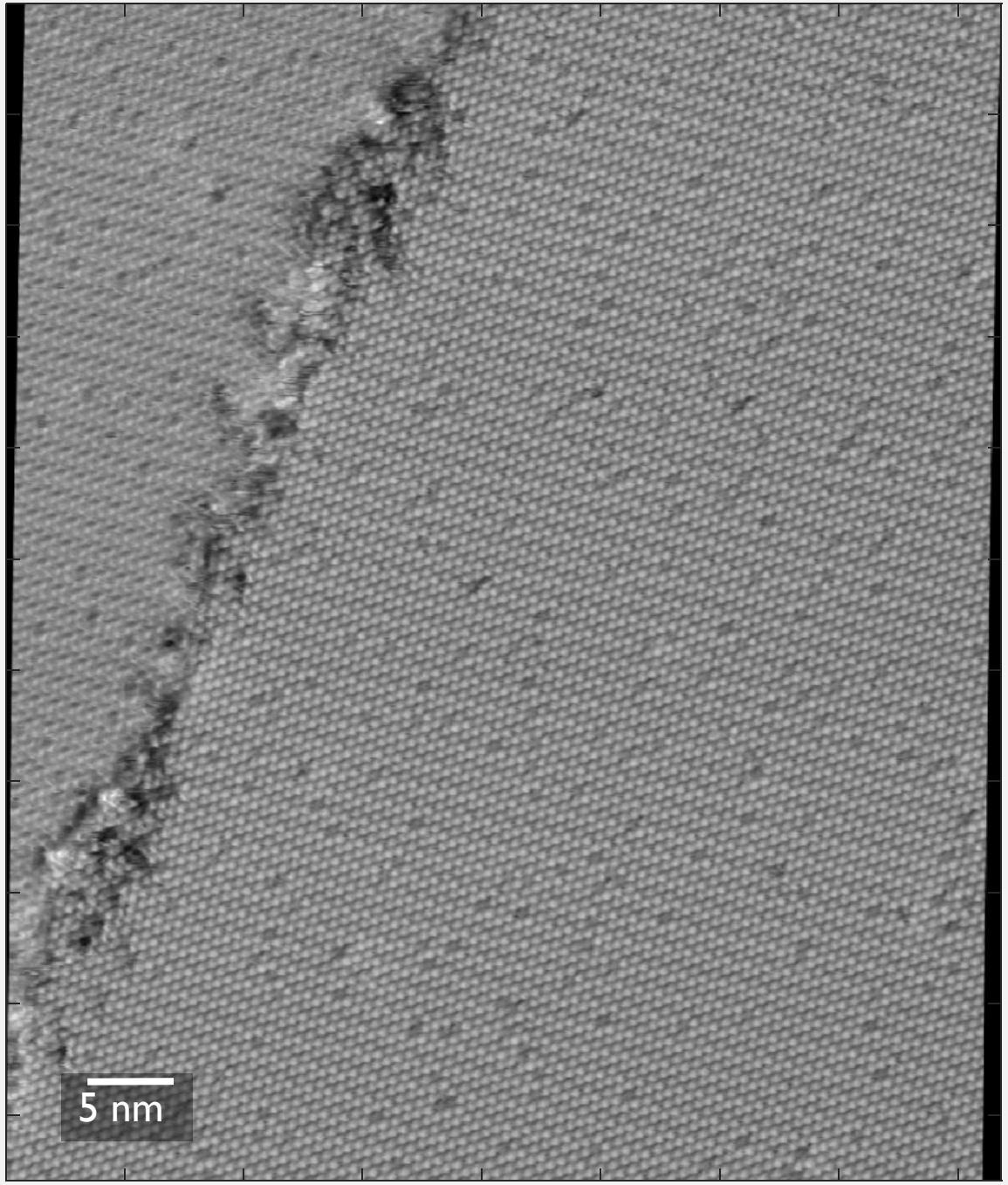
Normal Analysis

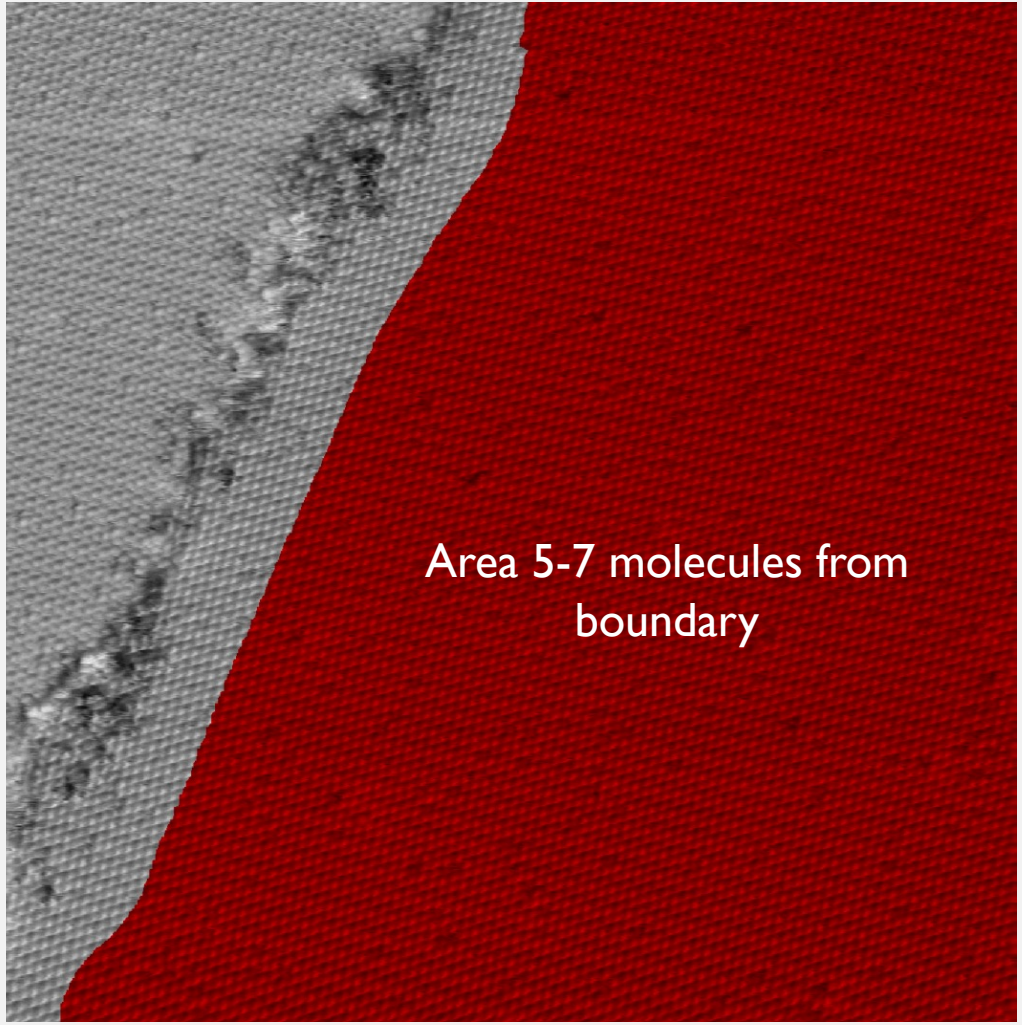


On-boundary Analysis

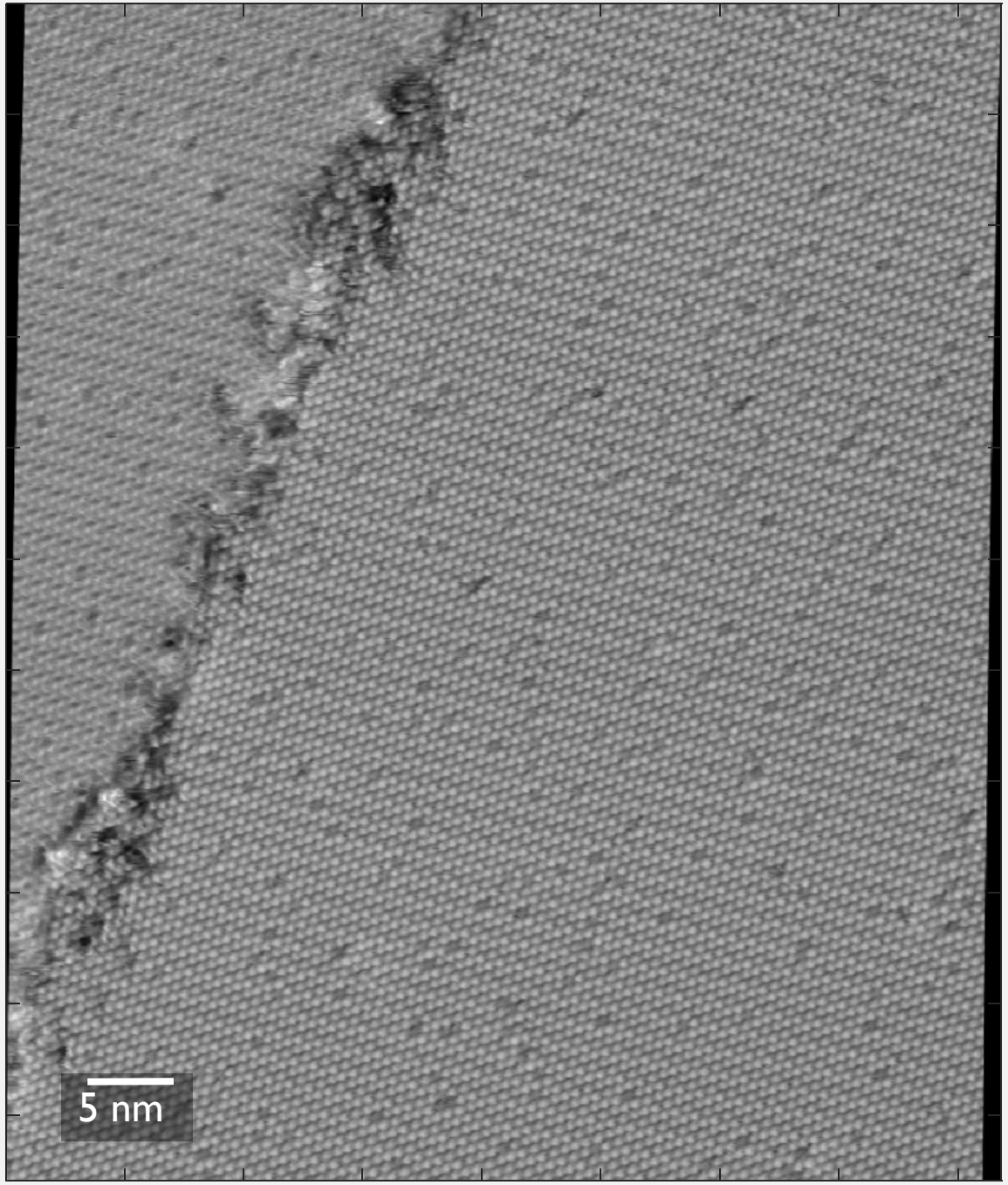


Offset plots





2019_07_17_0069
C8/C9 (2019 #6)



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C8/C9 (2019 #6)

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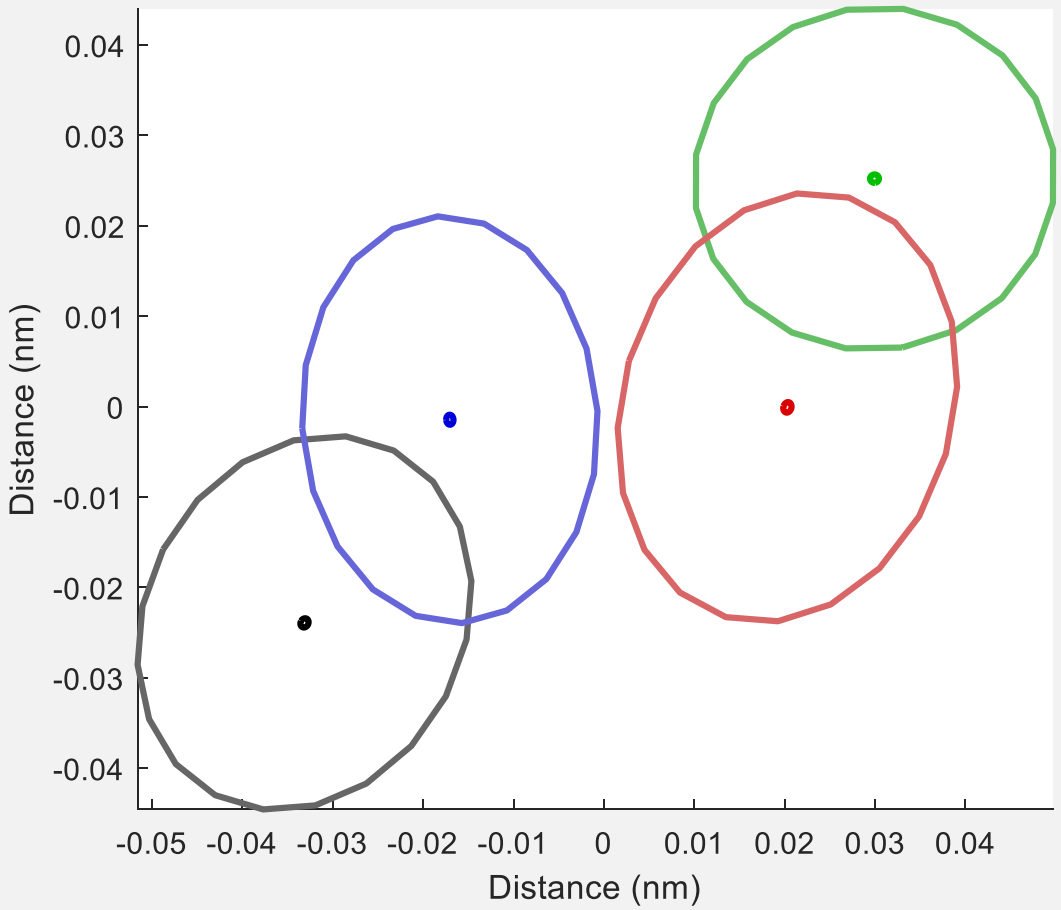
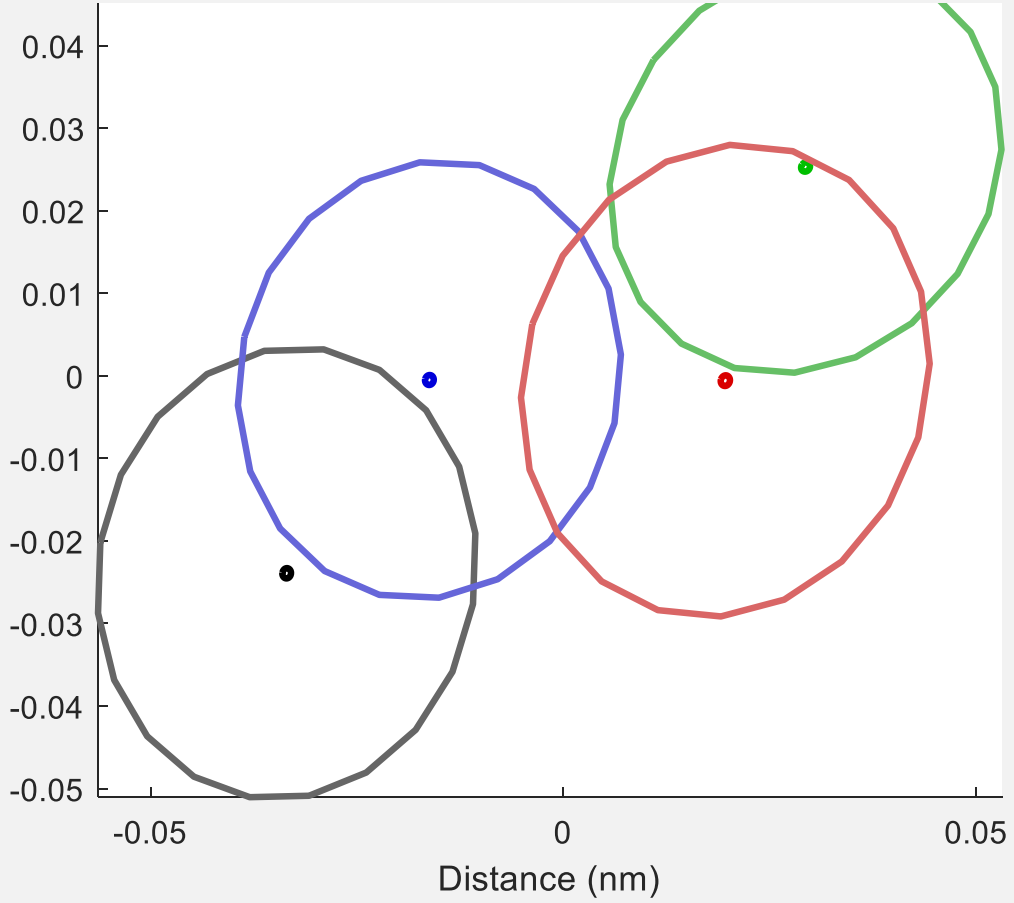


On-boundary Analysis



Offset plots

BOUNDARY ANALYSIS

- Confidence ellipses are larger
  - Increases the uncertainty
- Exclude molecules near the edge

MOTIVATION

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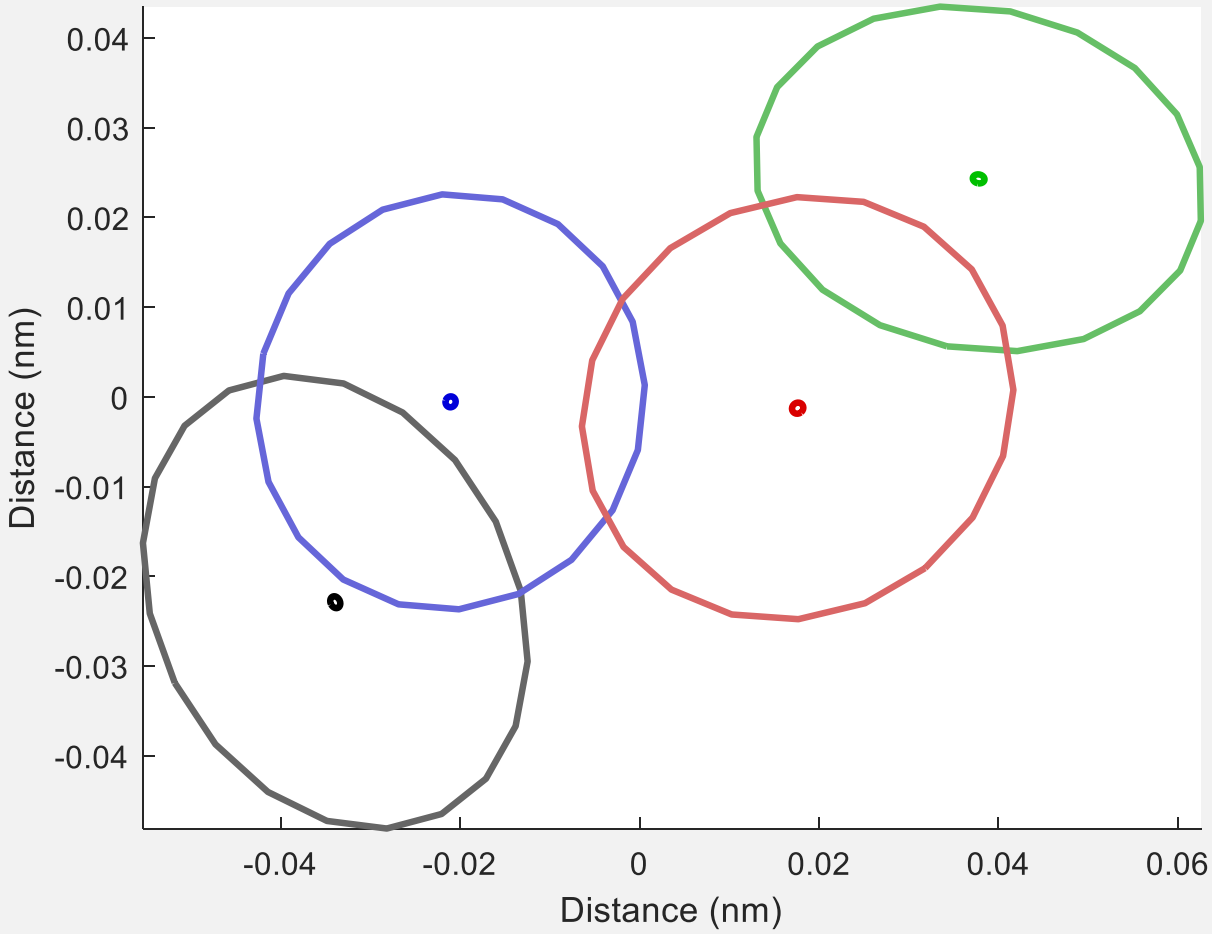
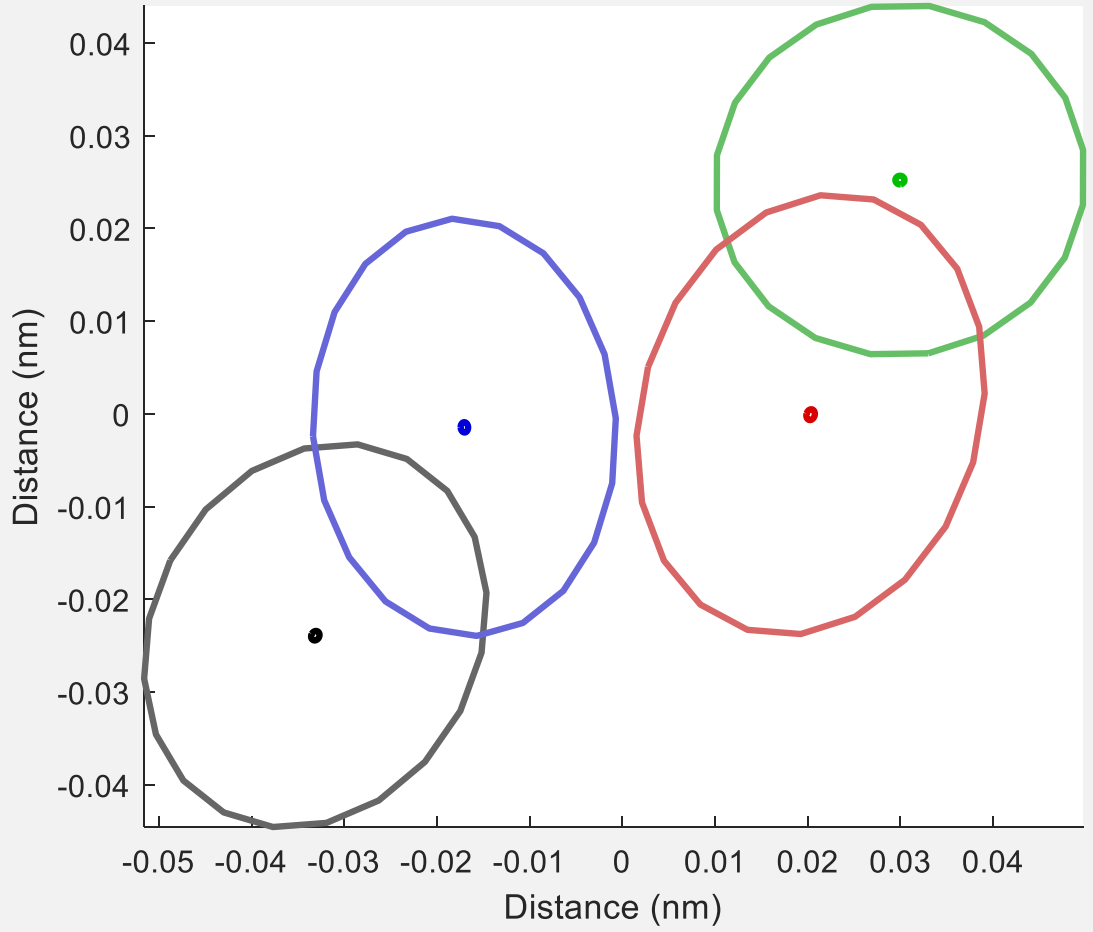
STRUCTURE COMPARISON – C9

2019_07_17_0061

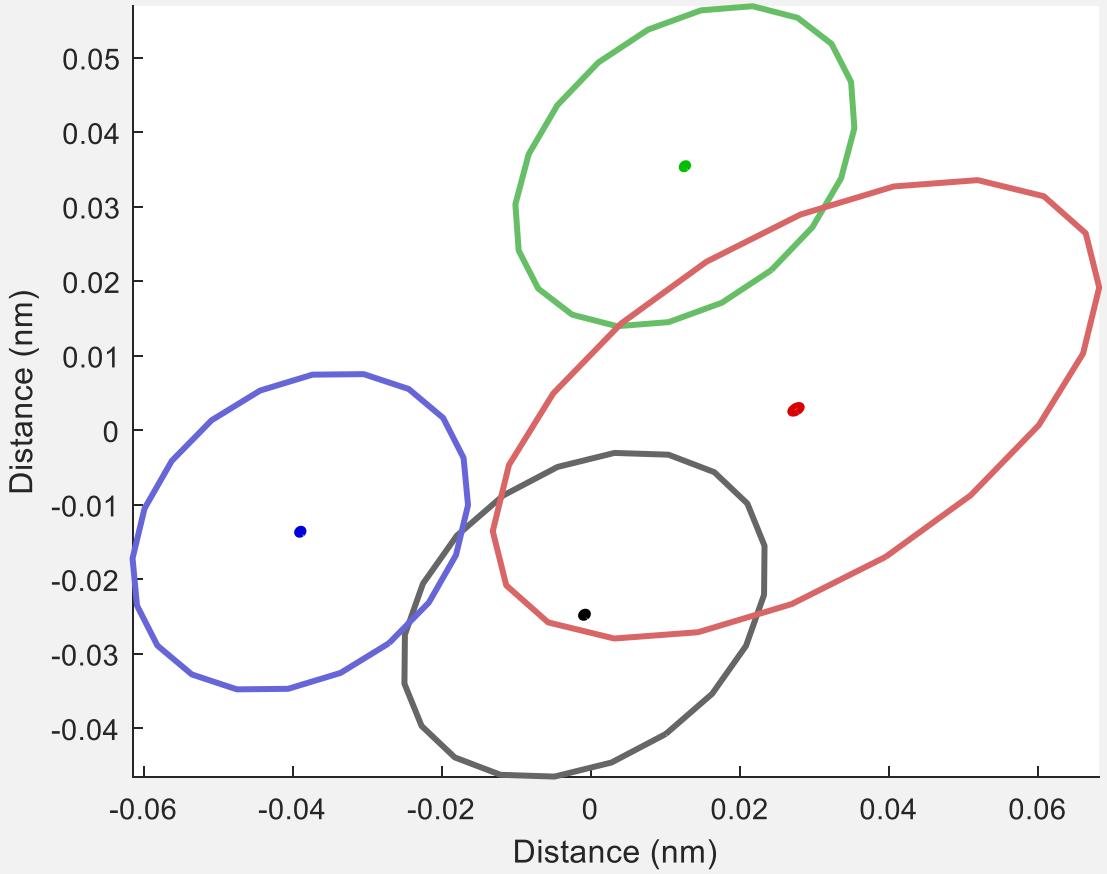


2019_07_17_0069

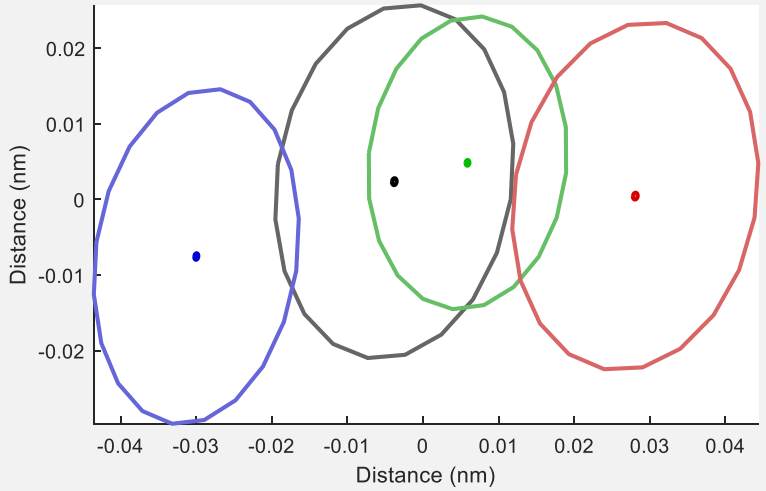


STRUCTURE COMPARISON – C10

2015_04_23_0009

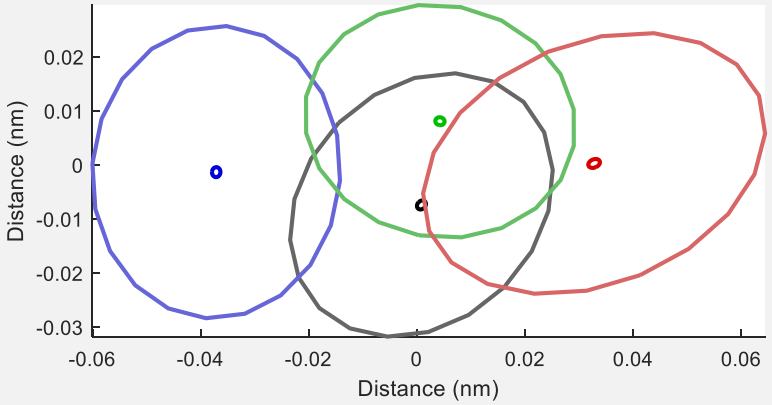


2015_03_03_0074

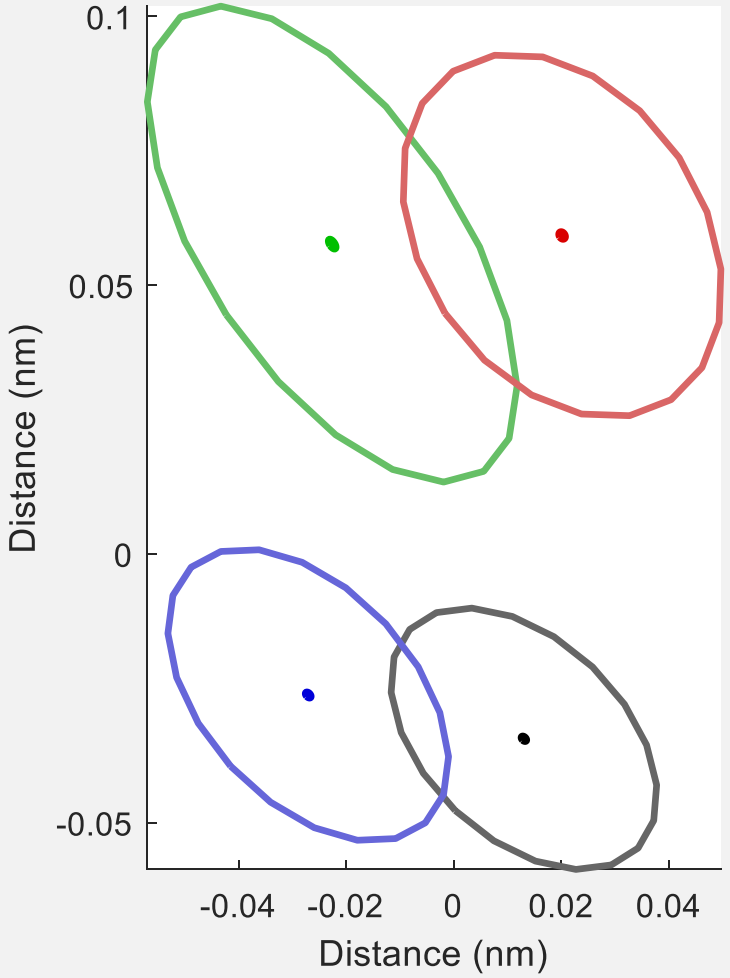


STRUCTURE COMPARISON – C10

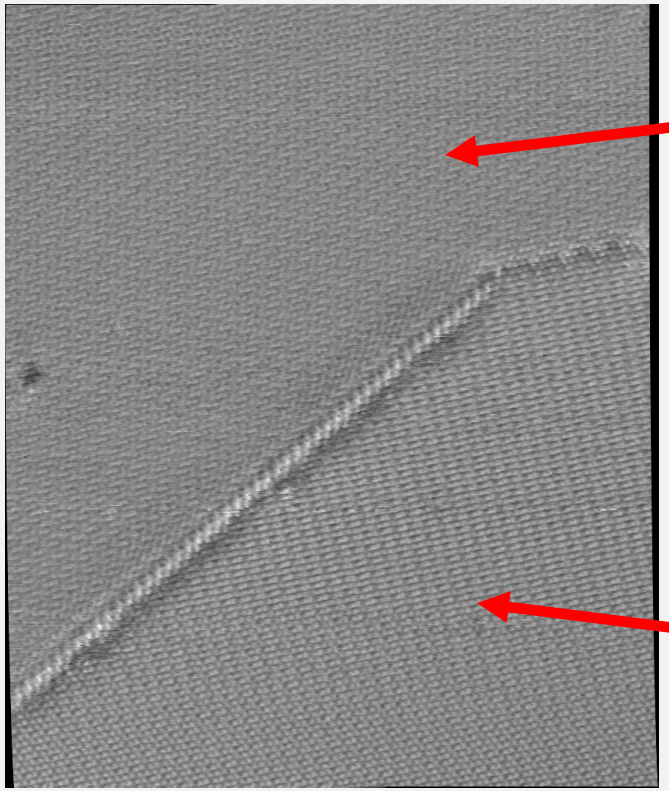
2015_04_15_0035



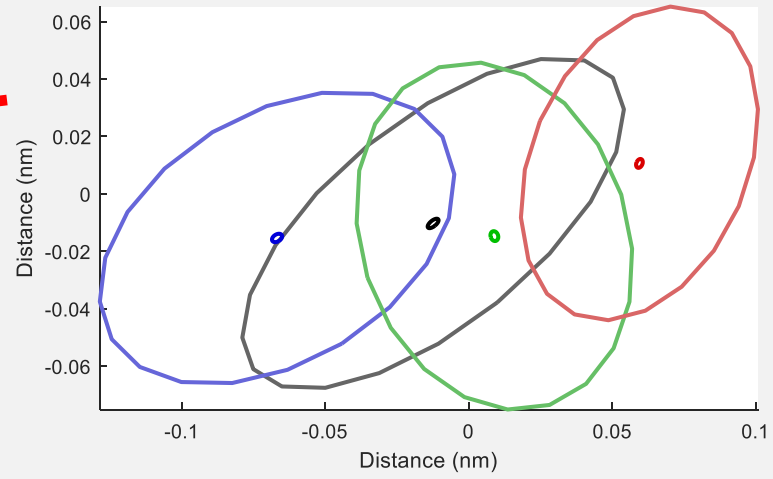
2018_04_02_0012

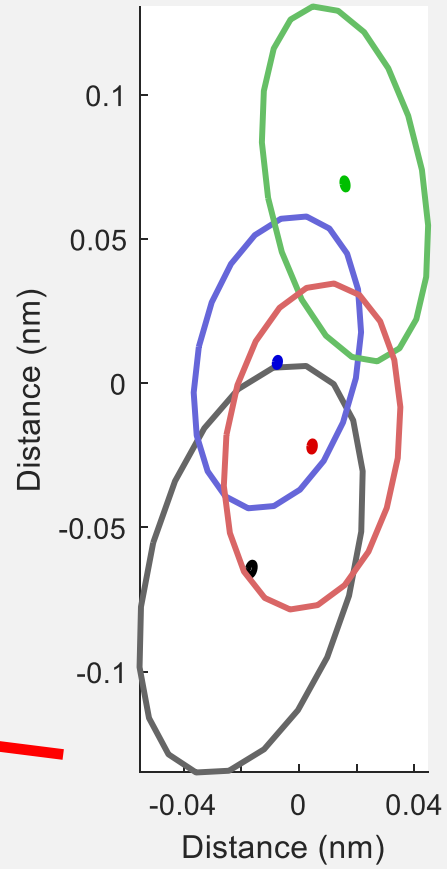


STRUCTURE COMPARISON – C10



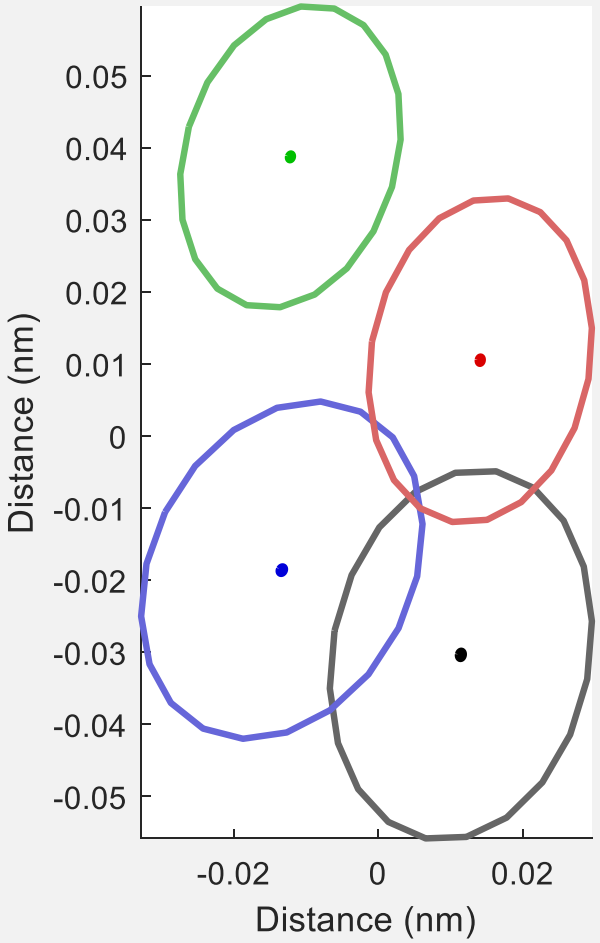
2019_06_12_0015



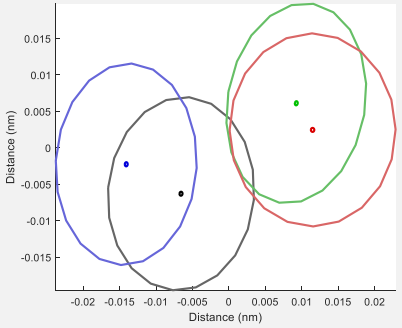


STRUCTURE COMPARISON – C10

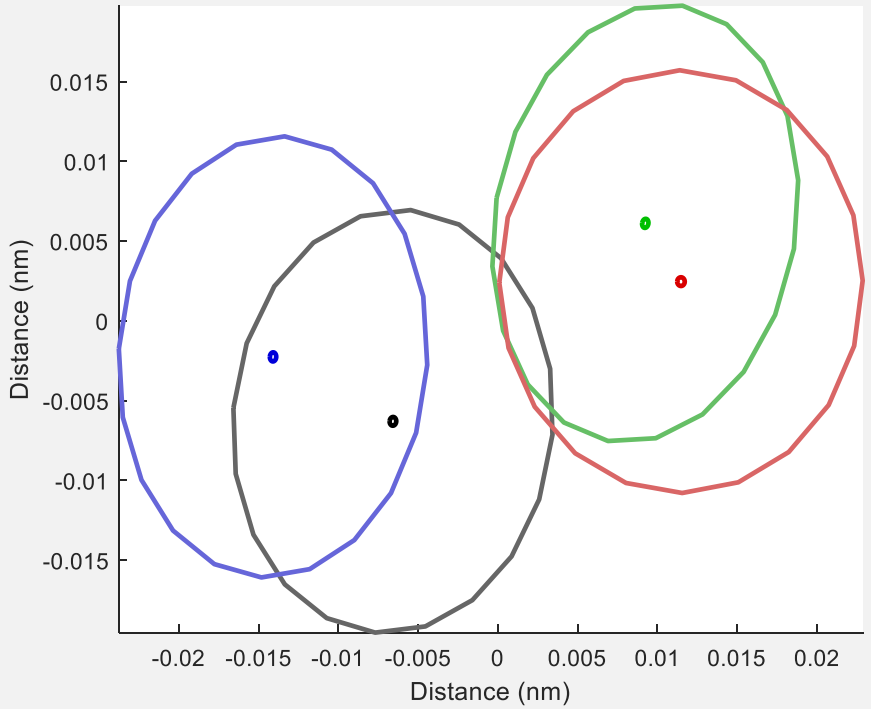
2019_06_17_0019



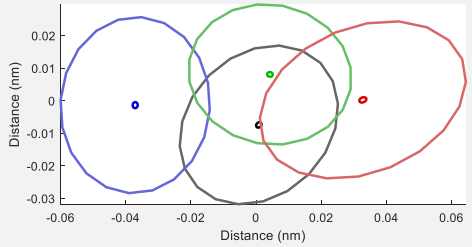
2019_06_17_0033

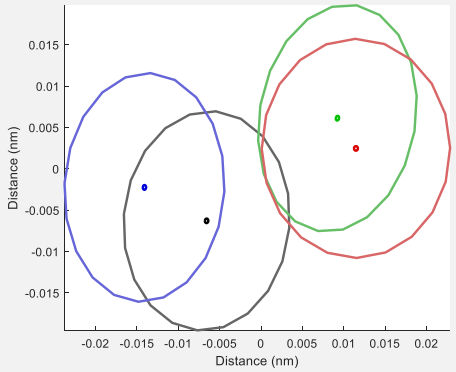


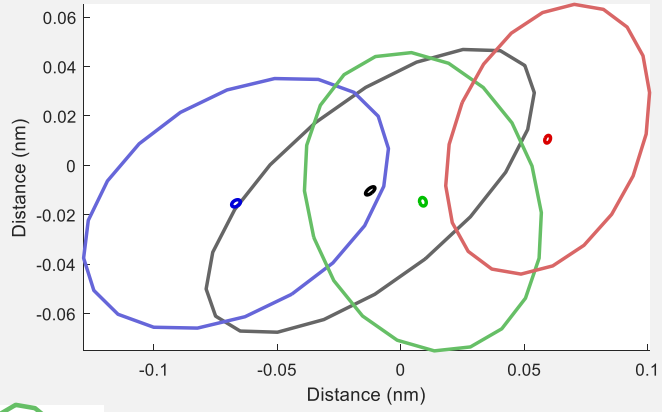
2019_06_17_0033 (bigger)

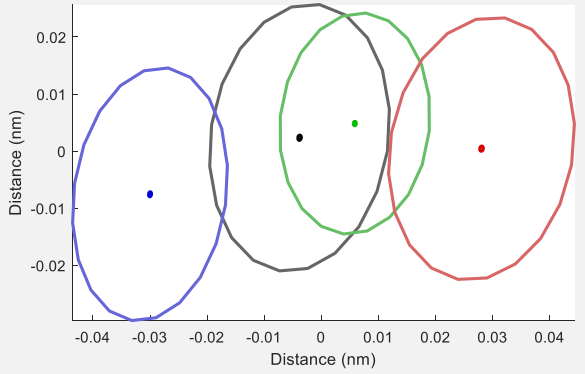


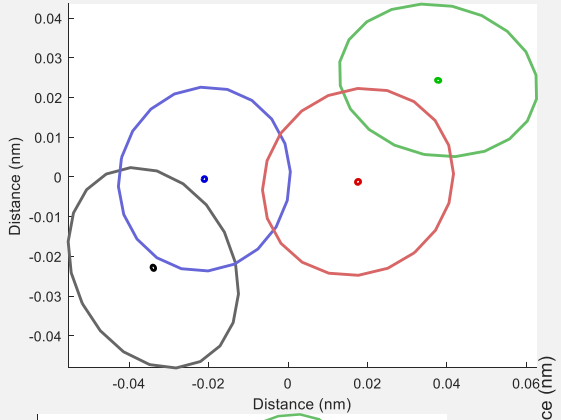
STRUCTURE COMPARISON

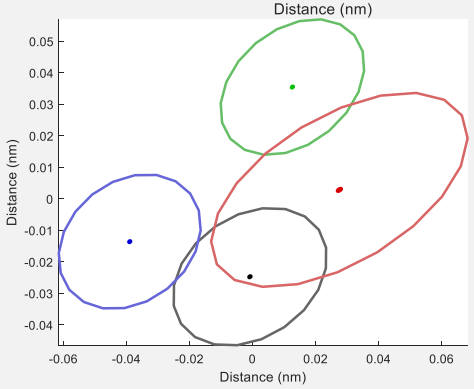


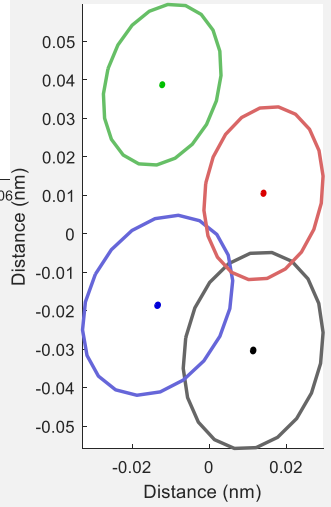


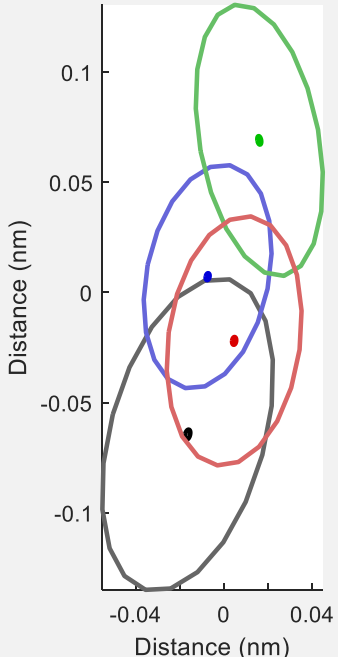


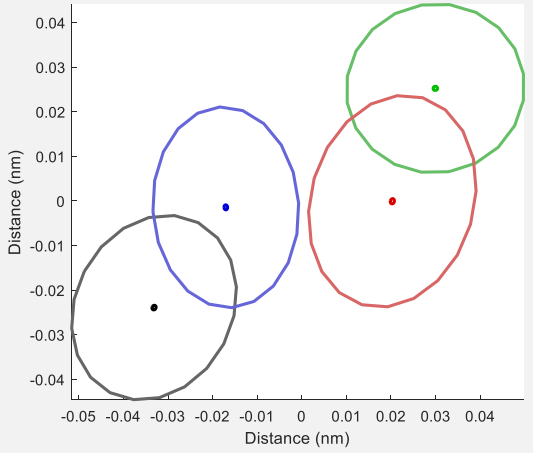


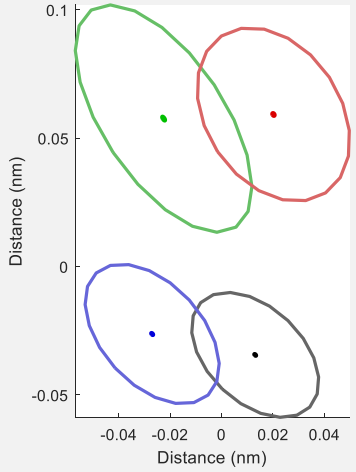




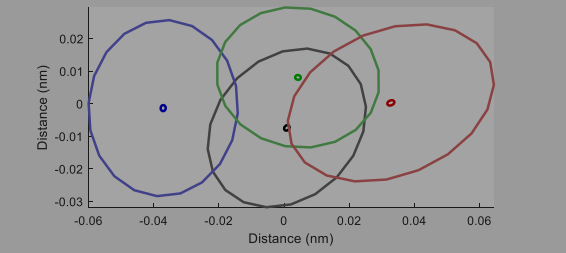


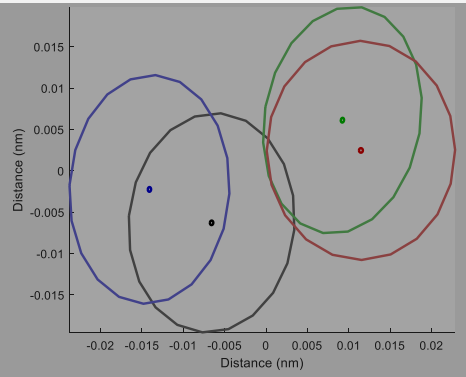


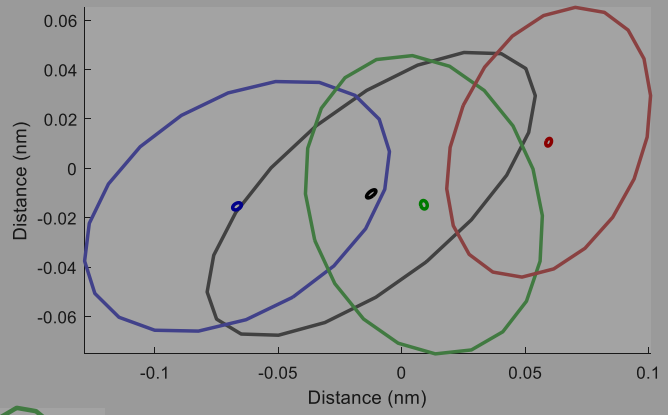


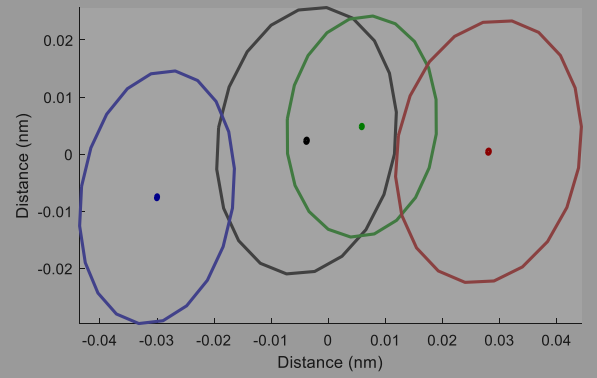


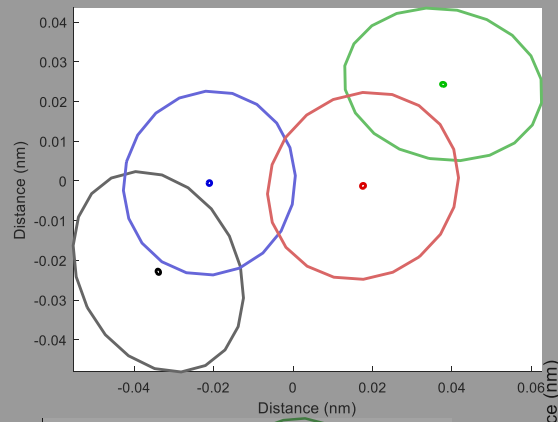
STRUCTURE COMPARISON

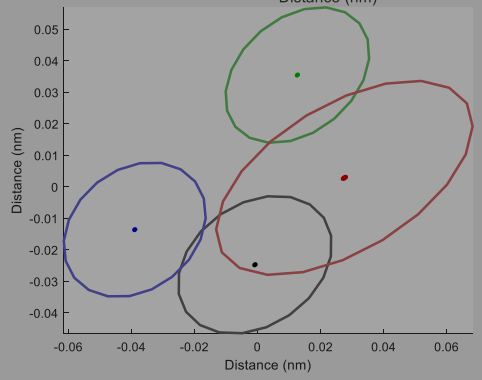


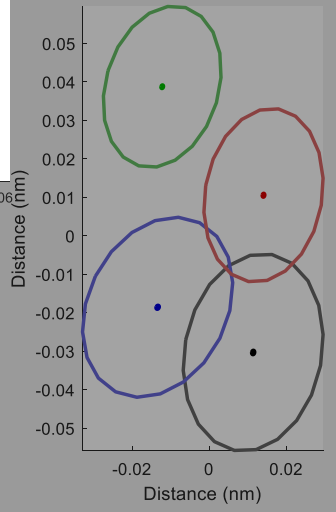


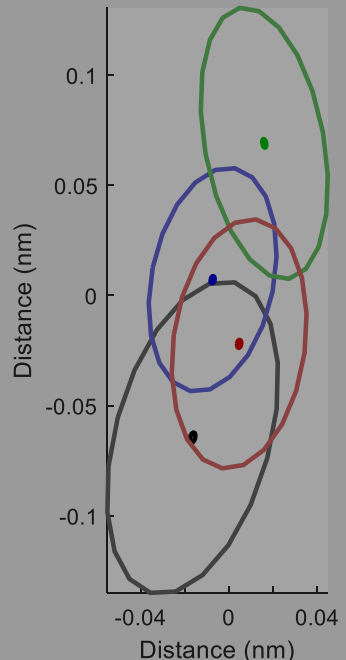


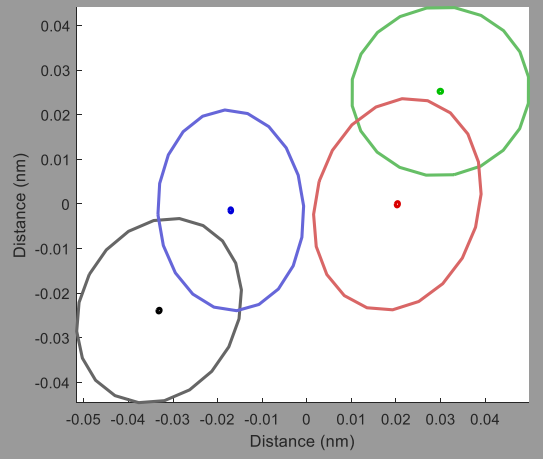


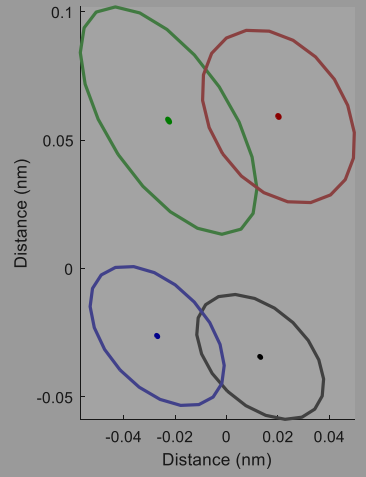












CONCLUSIONS AND FUTURE DIRECTION

- Made Alkanethiol SAM samples and imaged with STM
- Measured effects of proximity when analyzing images with boundaries and found noticeable effect
- Compared fingerprints of odd and even chain length SAMs and did not find a difference

ACKNOWLEDGMENTS

- Dr. Lloyd Bumm, Mitch Yothers, and Bumm group
- Dr. Abbott, Dr. Strauss, Amber Roepe, organizers
- National Science Foundation
- Nvidia