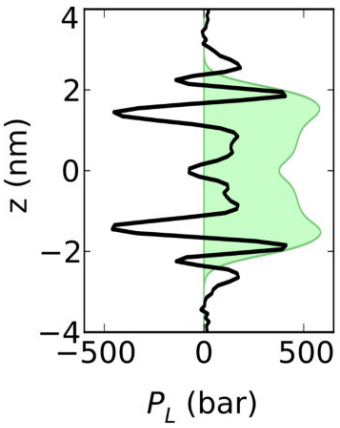
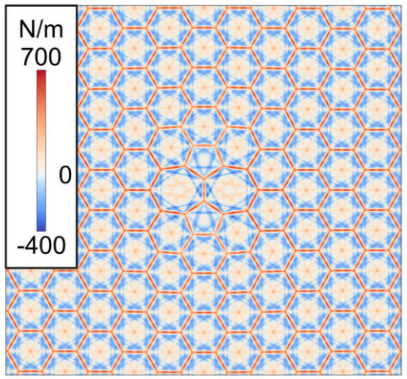
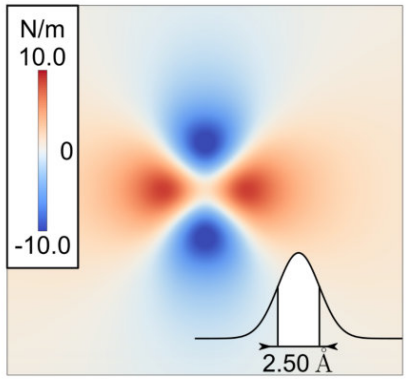
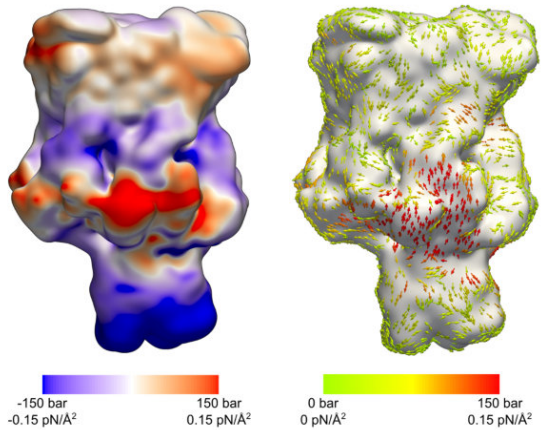




$(\sigma_{xx} + \sigma_{yy})/2$



$(\sigma_{xx} + \sigma_{yy})/2$



Is the Microscopic Stress from Molecular Simulations in Mechanical Equilibrium?

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Continuum Fields from Simulations

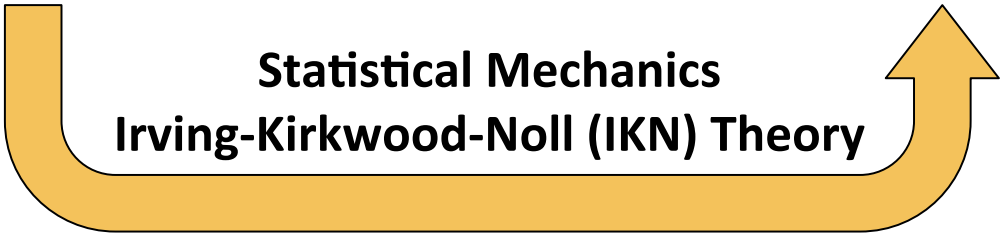
- Irving and Kirkwood (1950), and Noll (1955) developed a statistical mechanics framework to obtain continuum fields from particle-based systems through ensemble averaging

Classical Mechanics

$$\boldsymbol{F}^{\alpha} = m\boldsymbol{a}^{\alpha}$$

Continuum Mechanics

$$\rho\boldsymbol{a} = \rho\boldsymbol{b} + \nabla \cdot \boldsymbol{\sigma}$$



Microscopic Stress Tensor

$$\nabla \cdot \boldsymbol{\sigma}(\boldsymbol{x}) = \nabla \cdot \left(\sum_{\alpha=1}^{N} \langle m^{\alpha} \boldsymbol{v}^{\alpha} \otimes \boldsymbol{v}^{\alpha} \delta(\boldsymbol{r}^{\alpha} - \boldsymbol{x}) \rangle \right) - \sum_{\alpha=1}^{N} \langle \boldsymbol{F}^{\alpha} \delta(\boldsymbol{r}^{\alpha} - \boldsymbol{x}) \rangle \,,$$

Why Compute the Microscopic Stress?

- The microscopic stress field provides a connection between atomic/molecular interactions and macroscopic observables
  - Can be used to estimate elastic constants such as bending moduli
  - Quantify internal balance of forces due to defects or deformations
  - Powerful visualization tool to understand complex interactions in interfacial systems

An Ambiguous Definition of Stress

- The IKN procedure does not provide a unique definition of stress
  - Balance equations only define the divergence and not the field itself
  - Addition of a divergence-free field to the stress continues to satisfy linear momentum balance

$$\nabla \cdot \boldsymbol{\sigma}(\boldsymbol{x}) = \nabla \cdot \left(\sum_{\alpha=1}^{N} \left\langle m^{\alpha} \boldsymbol{v}^{\alpha} \otimes \boldsymbol{v}^{\alpha} \delta(\boldsymbol{r}^{\alpha} - \boldsymbol{x}) \right\rangle \right) - \sum_{\alpha=1}^{N} \left\langle \boldsymbol{F}^{\alpha} \delta(\boldsymbol{r}^{\alpha} - \boldsymbol{x}) \right\rangle ,$$

Decomposing Multi-body Potentials

- Non-uniqueness in the stress definition manifests itself when dealing with multi-body potentials

$$\boldsymbol{\sigma}(\boldsymbol{x}) = \boldsymbol{\sigma}_{\mathrm{K}}(\boldsymbol{x}) + \boldsymbol{\sigma}_{\mathrm{V}}(\boldsymbol{x}),$$

$$\boldsymbol{\sigma}_{\mathrm{K}}(\boldsymbol{x}) = -\left\langle \sum_{\alpha=1}^{N} m^{\alpha}\boldsymbol{v}^{\alpha} \otimes \boldsymbol{v}^{\alpha}\delta(\boldsymbol{r}^{\alpha} - \boldsymbol{x}) \right\rangle,$$

$$\boldsymbol{\sigma}_{\mathrm{V}}(\boldsymbol{x}) = \left\langle \sum_{\alpha,\beta>\alpha} \boldsymbol{f}^{\alpha\beta} \otimes \boldsymbol{r}^{\alpha\beta} B(\boldsymbol{r}^{\alpha}, \boldsymbol{r}^{\beta}; \boldsymbol{x}) \right\rangle,$$

Pairwise interaction force – not the net force on each particle – *i.e.,* forces must be decomposed

$$\boldsymbol{F}^{\alpha} = \sum_{\beta=1}^{N} \boldsymbol{f}^{\alpha\beta}$$

$$\boldsymbol{f}^{\alpha\beta} = -\boldsymbol{f}^{\beta\alpha}$$

Decomposed forces are not unique!

Bond function

$$\int_0^1 \delta[(1-s)\boldsymbol{r}^{\alpha} + s\boldsymbol{r}^{\beta} - \boldsymbol{x}]ds$$

Inter-particle distance

$$\boldsymbol{r}^{\alpha\beta} = \boldsymbol{r}^{\beta} - \boldsymbol{r}^{\alpha}$$

Force Decompositions

- Central force decomposition (CFD) – Admal and Tadmor (2010, 2011)
  - Requires decomposed forces to be central, *i.e.*, they must lie along the vector connecting the particles

$$\boldsymbol{f}^{\alpha\beta}_{\mathrm{CFD}} = \sum_{I=1}^{M} \frac{\partial \widetilde{V}_I}{\partial r^{\alpha\beta}} \frac{\boldsymbol{r}^{\alpha\beta}}{r^{\alpha\beta}}, \qquad V(\{\boldsymbol{r}^{\alpha}\}) = \widetilde{V}(\{r^{\alpha\beta}\}), \qquad \widetilde{V}(\{r^{\alpha\beta}\}) = \sum_{I=1}^{M} \widetilde{V}_I(\{r^{\alpha\beta}\})$$

  - Makes the resulting stress tensor symmetric by construction

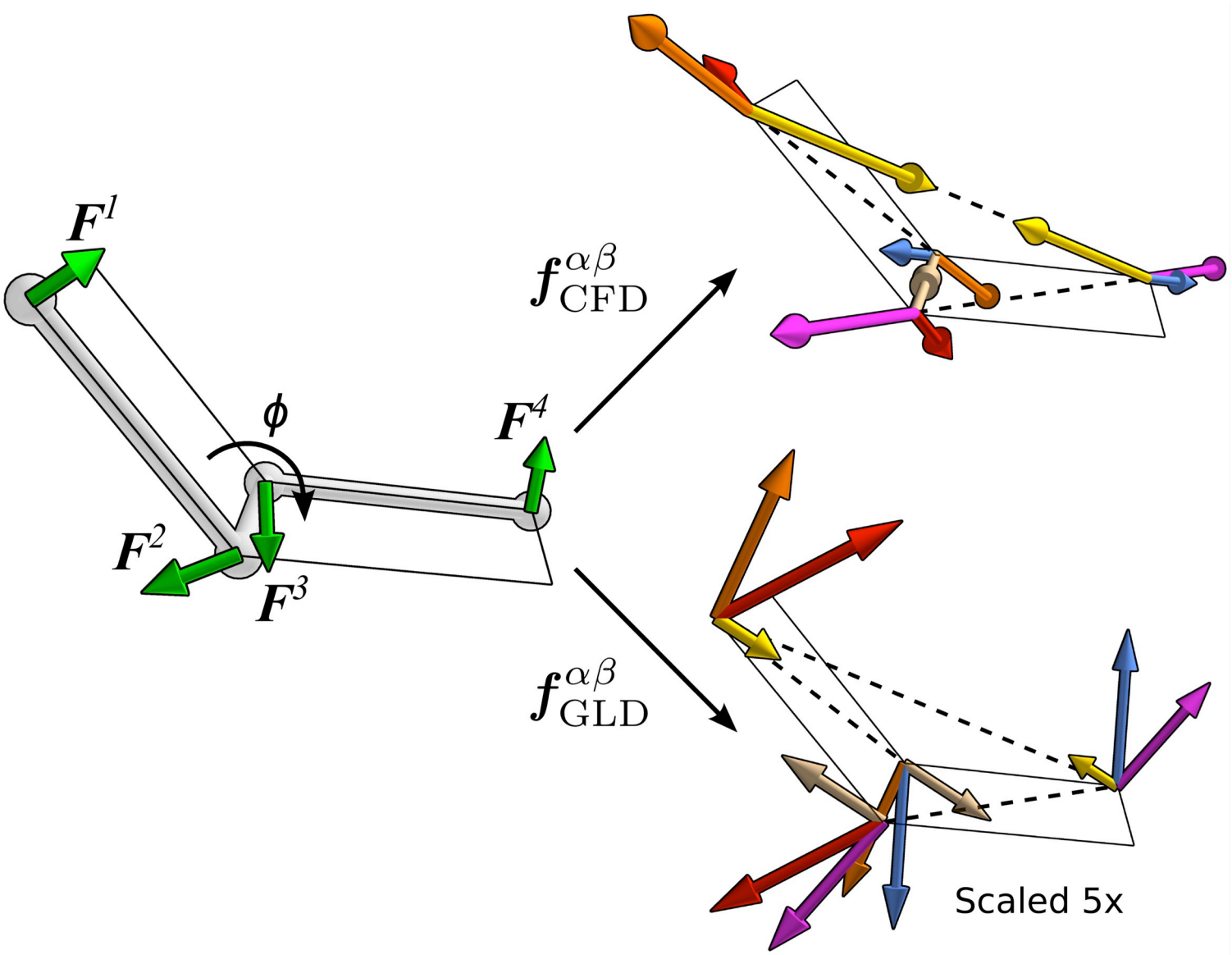
$$\boldsymbol{\sigma}_{\mathrm{V}}(\boldsymbol{x}) = \left\langle \sum_{\alpha,\beta>\alpha} \boldsymbol{f}^{\alpha\beta} \otimes \boldsymbol{r}^{\alpha\beta} B(\boldsymbol{r}^{\alpha}, \boldsymbol{r}^{\beta}; \boldsymbol{x}) \right\rangle$$

- Goetz-Lipowsky decompostion (GLD, 1999)

$$\boldsymbol{f}^{\alpha\beta}_{\mathrm{GLD}} = \sum_{I=1}^{M} \frac{1}{n_I} \left(\frac{\partial V_I}{\partial \boldsymbol{r}^{\beta}} - \frac{\partial V_I}{\partial \boldsymbol{r}^{\alpha}} \right)$$

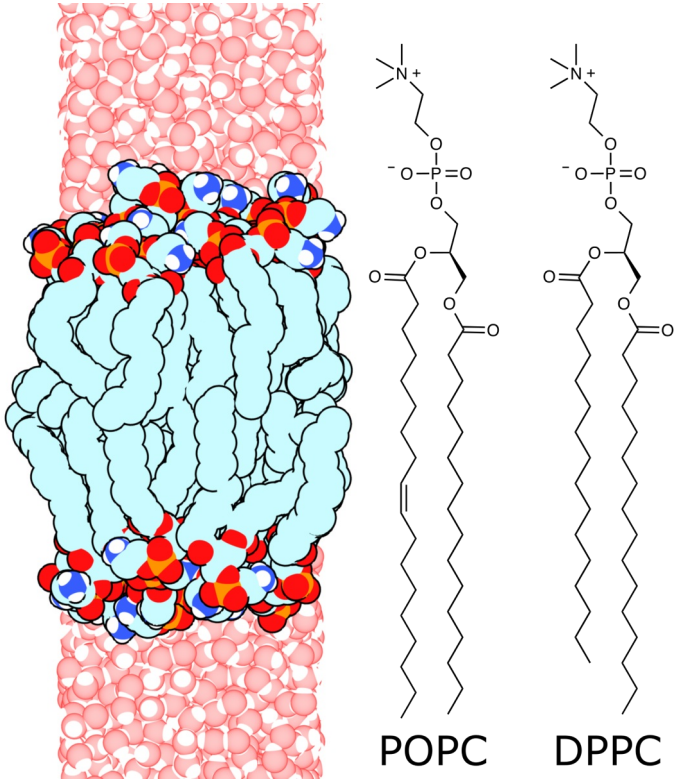
  - Natural decomposition, but may produce asymmetric stress

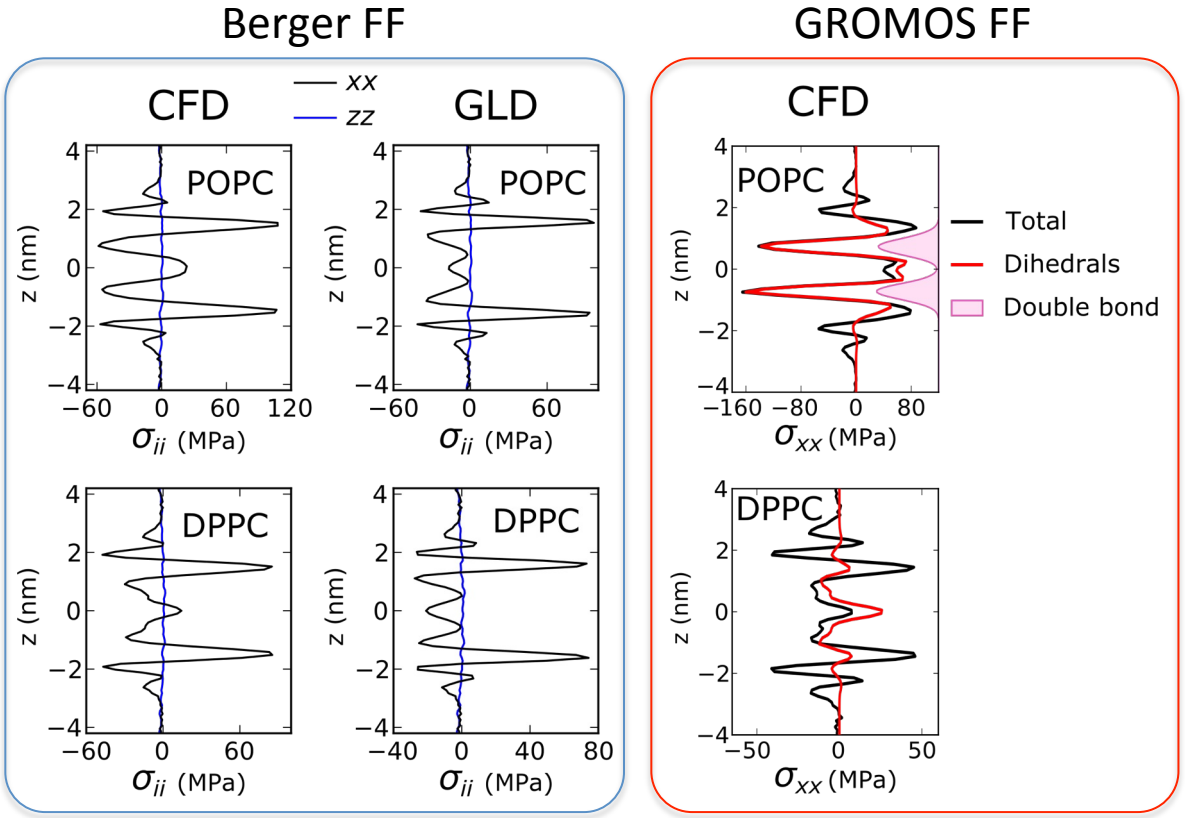
CFD vs GLD for a Dihedral Potential



Stress in Lipid Bilayer Membranes

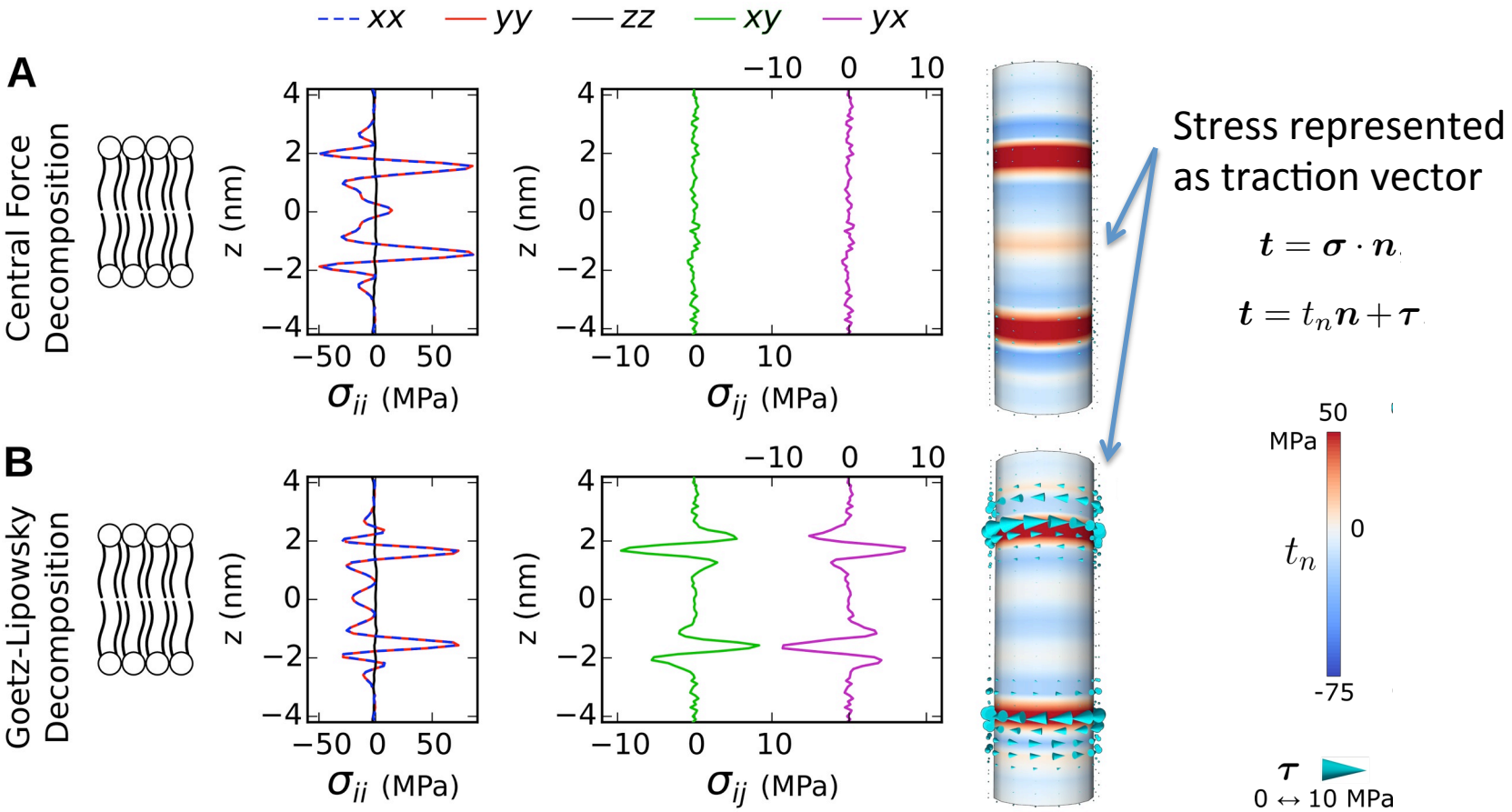
- Lipid molecules freely diffuse in the membrane plane, yet membrane is elastic in- and out-of-plane
- Highly symmetric system – stress is a function of membrane normal (z) only





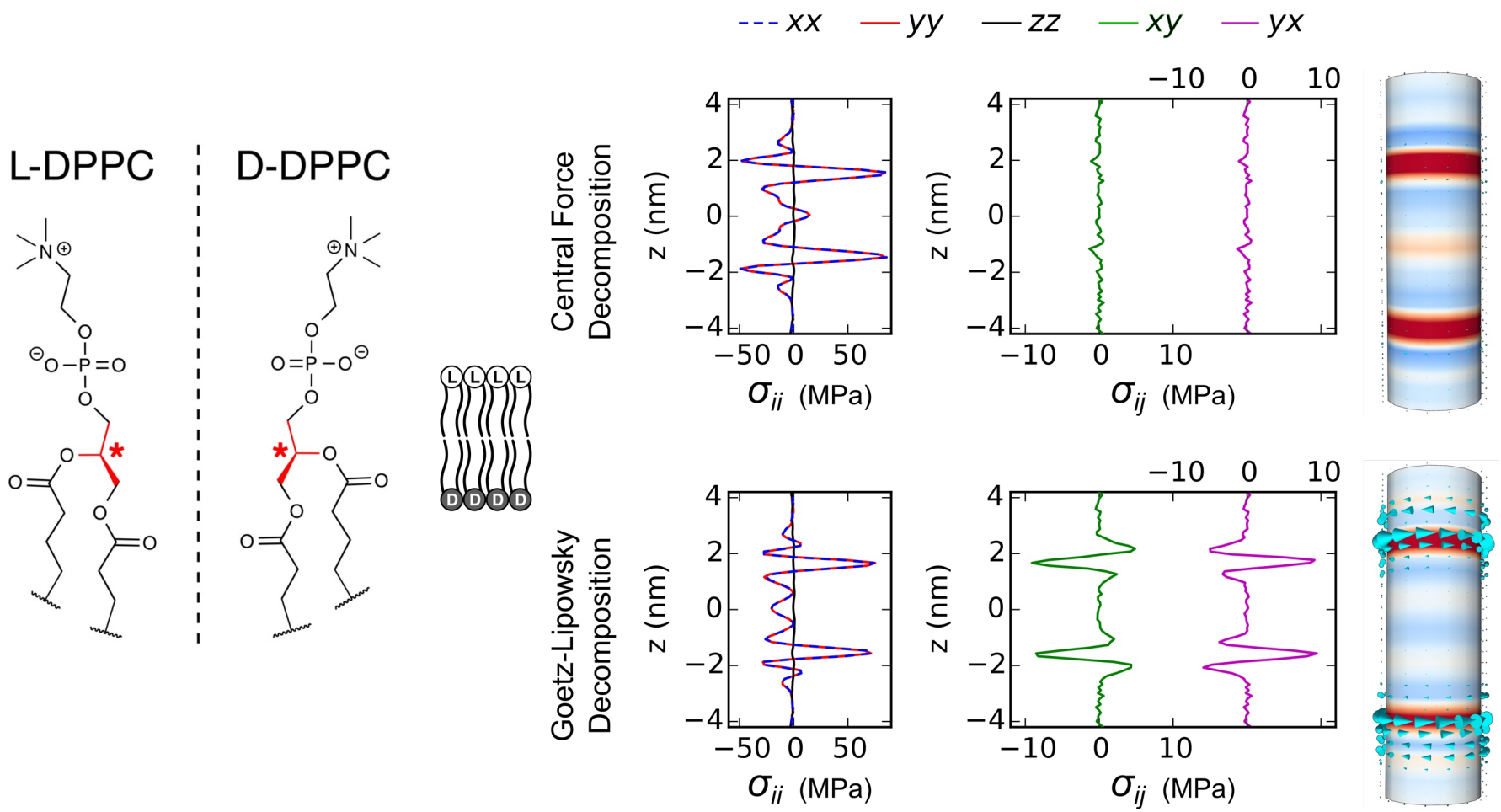
Non-Symmetric Stress

- GLD stress shows antisymmetric off-diagonal components, $\sigma_{xy} = -\sigma_{yx}$
  - GLD suggests internal distributed torques of opposing sign in each leaflet, but system is fluid (no shear) and equilibrated



GLD and Lipid Chirality

- Could lipid chirality be the source of the GLD torques?
  - Compared bilayers composed of lipids with opposing chirality



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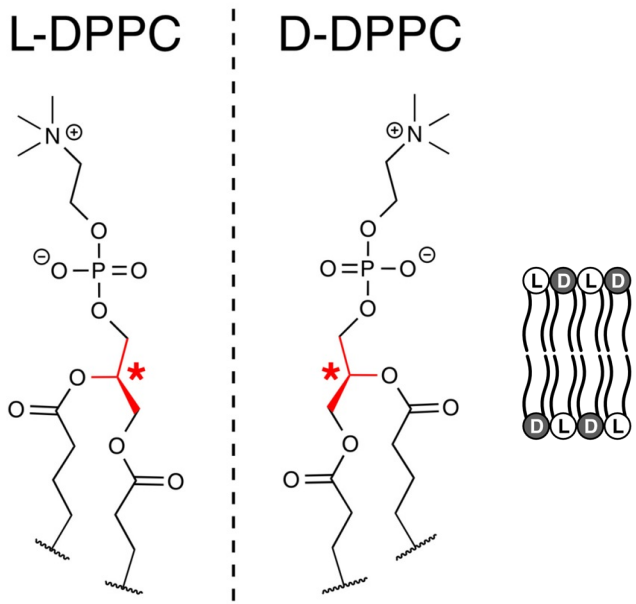
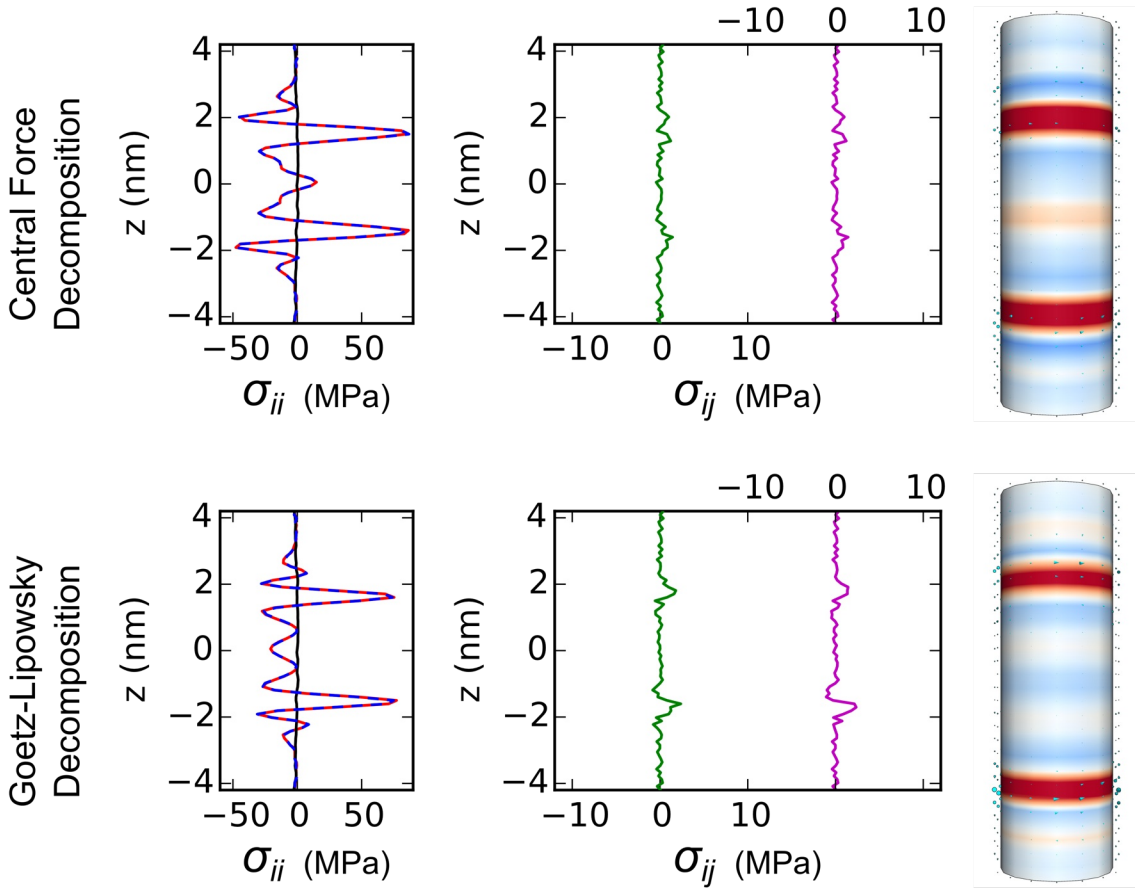




Which IKN Stress is Correct?

- Non-symmetric GLD stress violates conservation of angular momentum - no physical origin for the distributed torques
- CFD stress is symmetric by construction – satisfies conservation of linear of angular momentum
- What about elastic constants calculated from these stresses?
  - Bilayer gaussian modulus

$$\bar{\kappa} = \int \left[(\sigma_{xx} + \sigma_{yy})/2 - \sigma_{zz}\right] z^2 \; dz$$

$$\bar{\kappa}_{\mathrm{CFD}} = (-6.4, -6.7, -6.1) \cdot 10^{-20} \text{ J}$$

$$\bar{\kappa}_{\mathrm{GLD}} = (0.91, 0.57, 1.3) \cdot 10^{-20} \text{ J}$$

  - Gaussian modulus should be of the order of the negative bending modulus, experimentally $\sim 5 - 15 \cdot 10^{-20}$ J

Virial Stress per Atom

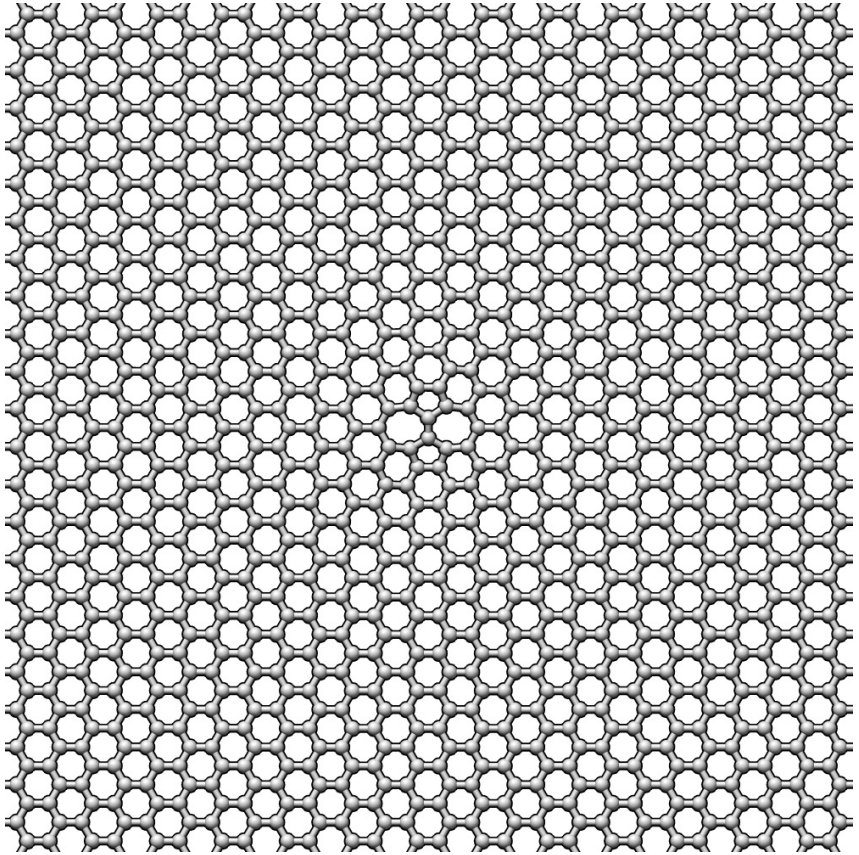
- For solid systems an alternative stress/atom has been proposed (Thompson, Plimpton, Mattson 2009)
  - Virial stress from a multibody potential is equally distributed among interacting particles

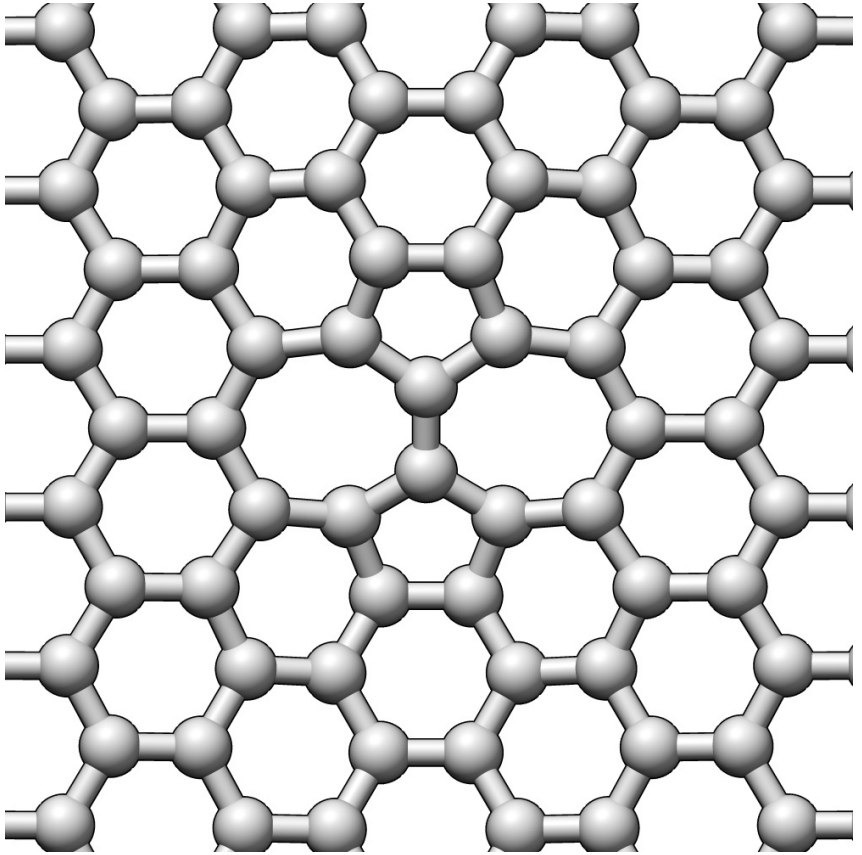
$$\boldsymbol{\sigma}_{\mathrm{V}}^{\alpha} = \frac{1}{\Omega_{\alpha}} \sum_{I \in \mathcal{I}^{\alpha}} \frac{1}{n_I} \left\langle \sum_{\beta} \frac{\partial V_I}{\partial \boldsymbol{r}^{\beta}} \otimes \boldsymbol{r}^{\beta} \right\rangle, \quad V = \sum_{I=1}^{M} V_I$$

  - Simple to calculate and unambiguous – can be used for any body potential
  - Physical interpretation has been questioned, but effective tool for visualization

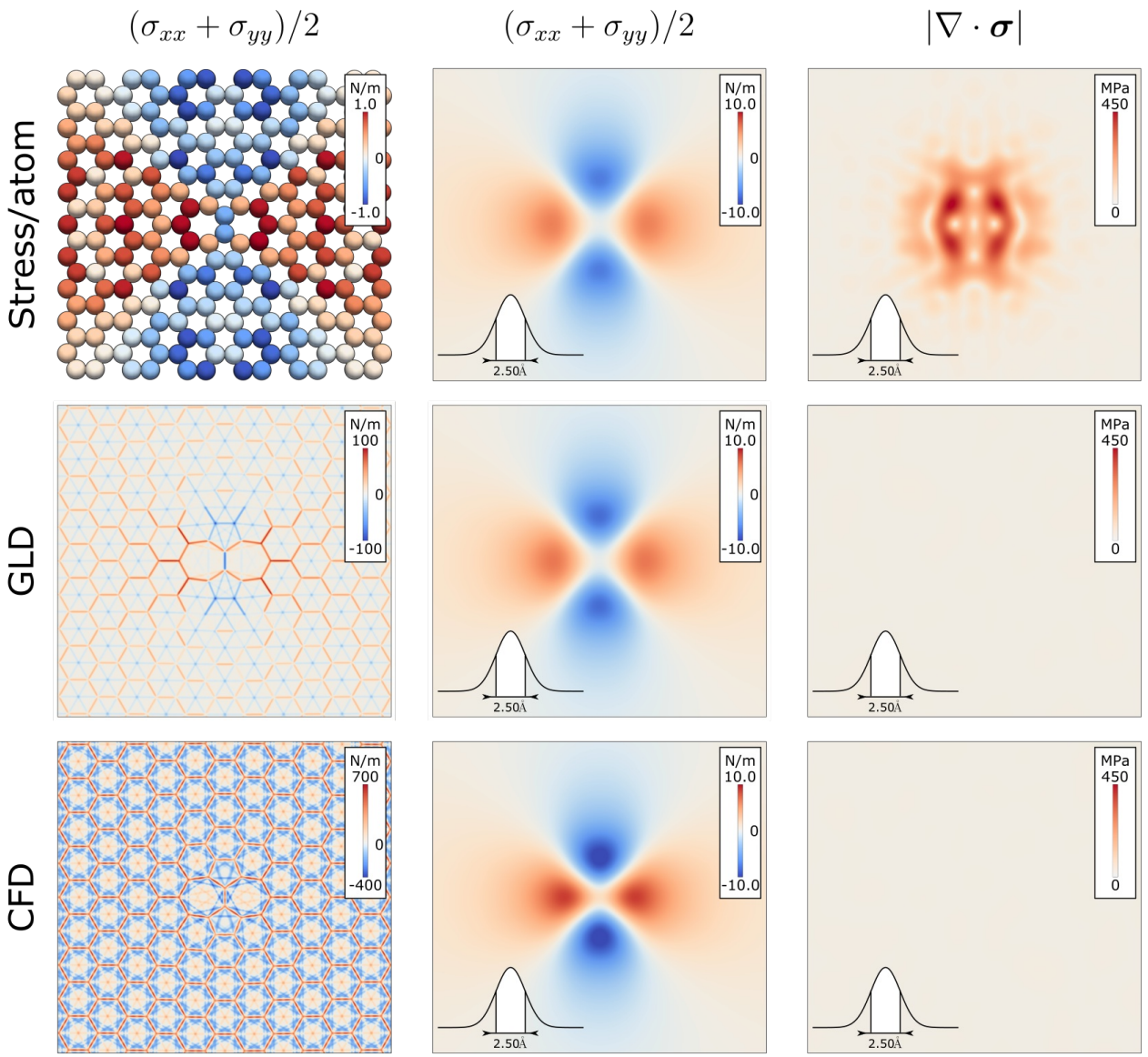
Graphene with Stone-Wales Defect

- How do the spatial IKN stresses compare to the stress/atom?
- Periodic graphene sheet with defect – morse bond potential + vdw, angle and dihedral terms (no charges)





Stress/atom vs IKN Spatial Stress



Stress/atom vs IKN Spatial Stress

- Virial stress/atom shows non-zero divergence near defect – violates conservation of linear momentum
- All stresses are qualitatively similar when spatially averaged using gaussian kernel
  - Virial stress/atom is computationally much faster – may be used with caution as a quick visualization tool
- Magnitude of the raw stresses is significantly different

CFD and n-body Potentials

- IKN + CFD provides a consistent and physically meaningful stress but has an important limitation
  - CFD is uniquely defined only for potentials with up to 4 interacting particles (e.g., dihedrals)
  - For 5-body and higher order potentials the system is underdetermined and many possible CFDs exist
  - $\frac{\partial \widetilde{V}_I}{\partial r^{\alpha\beta}}$ requires an arbitrary extension of potential beyond defined configurational space

A Geometric Definition of Stress

- Stress can be defined from covariance arguments similar to Doyle-Ericksen equation of continuum mechanics

$$\boldsymbol{\sigma}(\boldsymbol{x}) = \frac{2}{\sqrt{g(\boldsymbol{x})}} \frac{\delta A}{\delta \boldsymbol{g}(\boldsymbol{x})}$$

Variation of the canonical free energy

Infinitesimal change of metric due to a change of coordinates (*i.e.*, a deformation)

- Resulting potential term is analogous to the IKN expression

$$\boldsymbol{\sigma}_V(\boldsymbol{x}) =$$

$$= \sum_{I=1}^{M} \sum_{\alpha,\beta>\alpha} \left\langle \left(\nabla_{\mathcal{S}_{I_n}} \widetilde{V}_{I_n} \right)_{\alpha\beta} \frac{\boldsymbol{r}^{\alpha\beta} \otimes \boldsymbol{r}^{\alpha\beta}}{r^{\alpha\beta}} B(\boldsymbol{r}^{\alpha}, \boldsymbol{r}^{\beta}; \boldsymbol{x}) \right\rangle$$

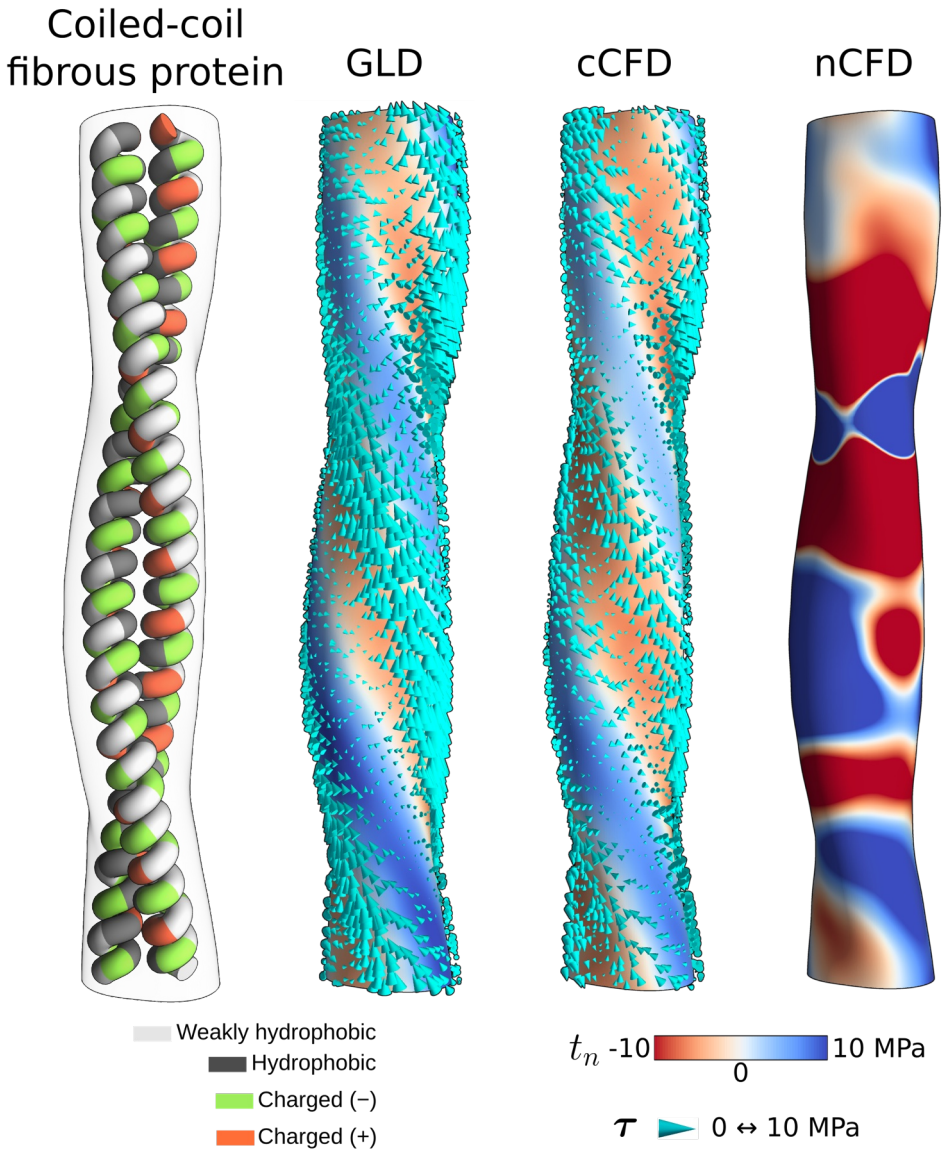
$$= \frac{1}{2} \left\langle \sum_{\alpha,\beta\neq\alpha} \boldsymbol{f}^{\alpha\beta} \otimes \boldsymbol{r}^{\alpha\beta} B(\boldsymbol{r}^{\alpha}, \boldsymbol{r}^{\beta}; \boldsymbol{x}) \right\rangle,$$

$$\boldsymbol{f}^{\alpha\beta}_{\mathrm{cCFD}} = \sum_{I=1}^{M} \left(\nabla_{\mathcal{S}_I} \widetilde{V}_I \right)_{\alpha\beta} \frac{\boldsymbol{r}^{\alpha\beta}}{r^{\alpha\beta}}$$

Covariant central force decomposition (cCFD)

cCFD and 5-body Potentials

- For up to 4-body potentials CFD and cCFD coincide
- cCFD is unique for any n-body potential
- Example: fibrous coiled-coil protein (infinitely periodic) simulated with 5-body potential term (CHARMM22/CMAP)



Summary

- We show that non-uniqueness in definition of the microscopic stress has profound effects in resulting continuum fields
- Comparison of various force decompositions of multibody potentials show that CFD and cCFD produce physically meaningful stresses
- We present a covariant central force decomposition that can be used to uniquely decompose any n-body potential

Numerical Implementation

- All stress calculations were done with custom version of GROMACS v4.5.5
- We have also implemented an independent C++ library called libMDStress that can be incorporated into any molecular simulation code to compute local stresses including the various IKN flavors + virial stress/atom
- Code available from mdstress.org

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5. Tadmor, E. B. & Miller, R. E. Modeling Materials: Continuum, Atomistic and Multiscale Techniques. (**2011**)