Mechanical Properties of Glassy Polymer Nanocomposites via Atomistic and Continuum Models: The Role of Interphases

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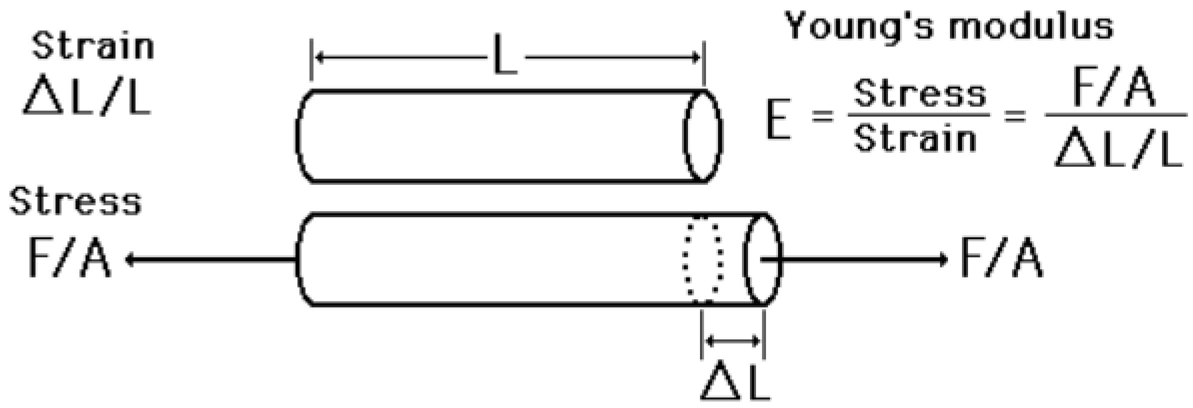
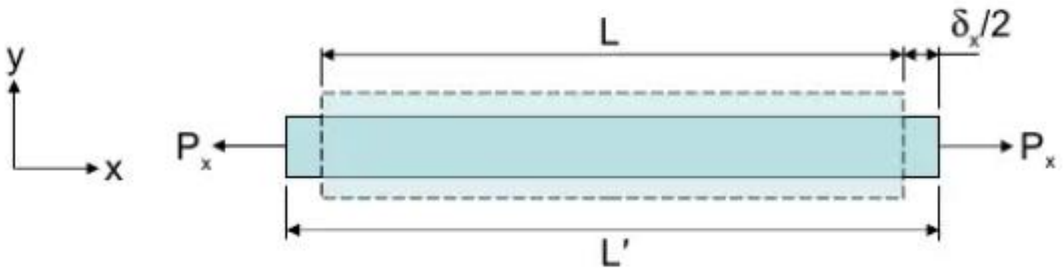
Young Modulus and Poison ratio

Young Modulus



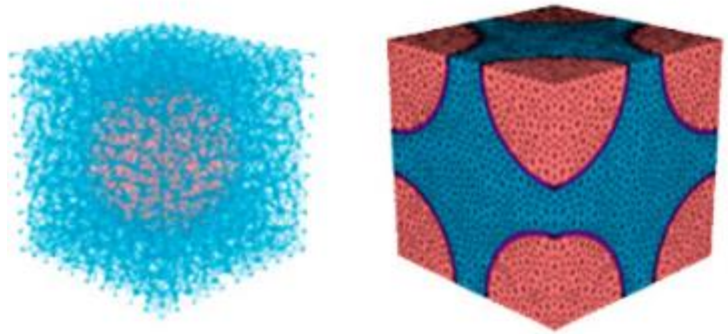
The Young modulus is the ration between the stress to the strain

Poisson ration



Poisson ratio is the ratio between the axial elongation to the lateral contraction

Case of heterogenoeus material??

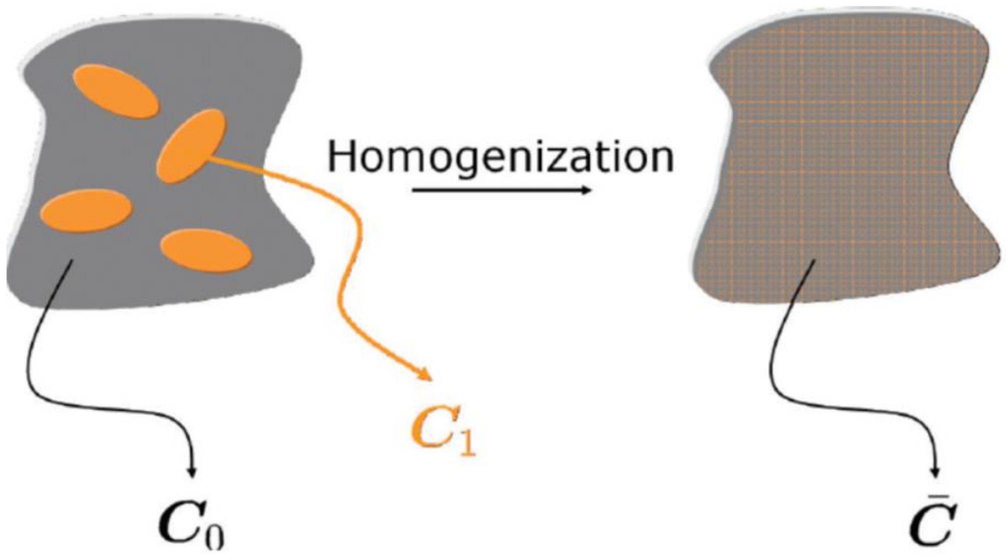


E and ν??

Homogenization theory

- Replace the initially heterogeneous medium within an identified representative volume element (RVE in short) by an effective homogeneous medium at the macroscopic scale having the same mechanical behavior

C_i is the rigidity matrix of the constituents



$\tilde{C}$ is the effective rigidity

Heterogeneous material: Micro-level defined by **y** positon

Homogeneous material: Macro-level defined by **x** positon

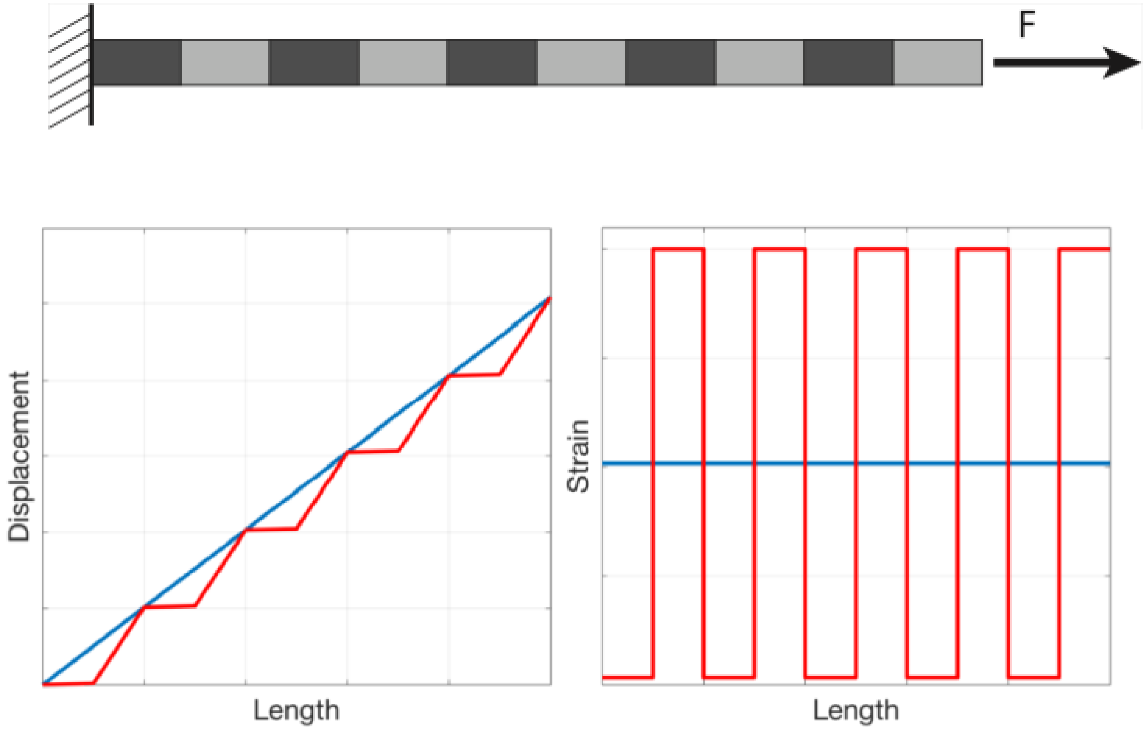
- The effective medium (homogenized medium) at Macroscopic scale can be :

a) Cauchy type : Displacement is the only degree of freedom

The constitutive law is given by Hooks Law as:

$$\sigma = C\ E$$

σ and E are uniform distributed within the medium

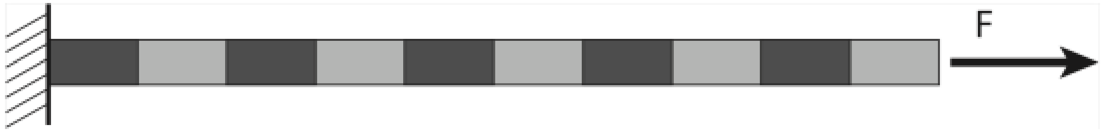


σ is the stress

E: Macroscopic deformation (E(x)=cte)

- The effective medium (homogenized medium) at Macroscopic scale can be :

b) Second gradient type : Displacement and gradient of displacement are the degree of freedom

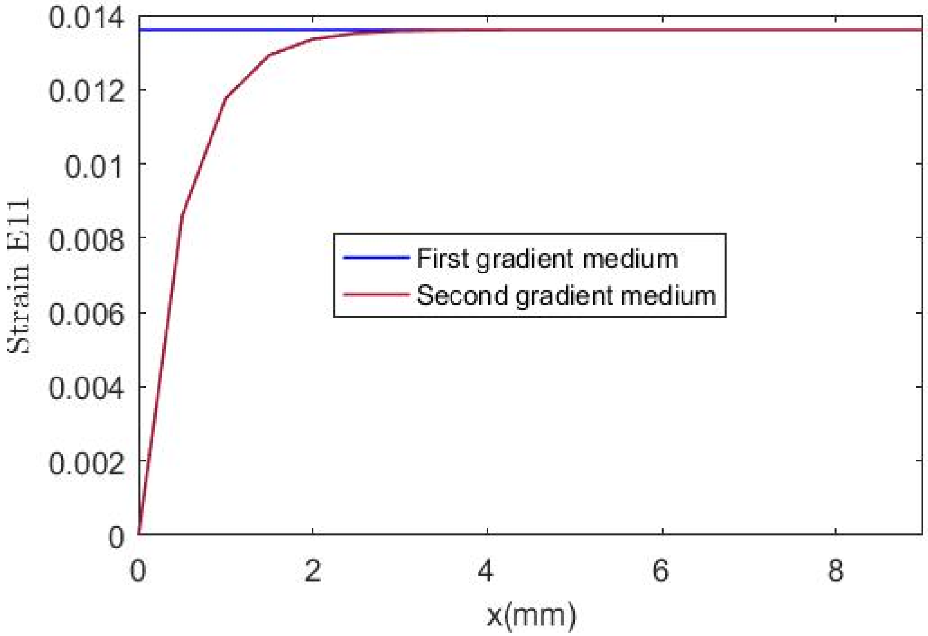


The constitutive law is given by Hooks Law as:

$$\sigma_{11} = \sigma_0 = C^{hom}{}_{11} E_{11} + B^{hom}{}_{11} \frac{dE_{11}}{dx} \rightarrow E_{11} = \frac{\sigma_0}{C^{hom}{}_{11}} \left(1 - \exp^{-\frac{C^{hom}{}_{11}}{B^{hom}{}_{11}} x} \right)$$

σ (x) and E (x) are depend on the position x within the medium

$$\sigma = C\ E + BK$$
$$S = B\ E\ + AK$$



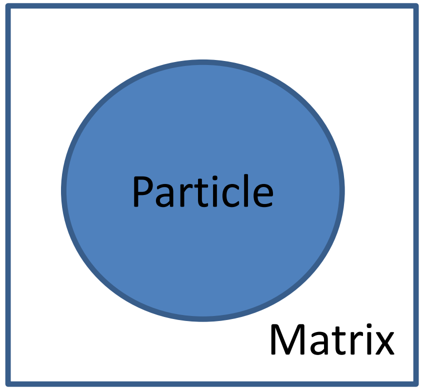
K: Gradient of deformation, S: Hyper stress

B: Coupling rigidity matrix and A: SG rigidity matrix

Homogenization

- The heterogeneous medium can be modeled as :

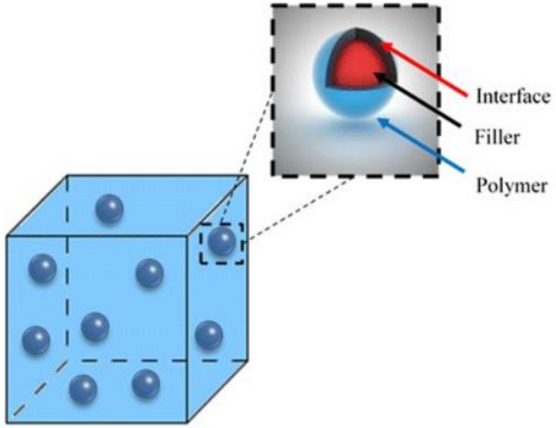
a) **2 phases model**: Mechanical properties of two-phase composite materials are obtained in terms of the particle and the matrix volume fraction and geometry **without** considering the **interphase** zone.



Moritanaka Model (Analytical):

$$C = \left(\left(V^m C^m + V^{NP} C^{NP} T\right)\left(V^m I + V^{NP} T\right)\right)^{-1}$$

b) **Three phases model**: The reinforcement and adjacent polymer region cannot be accurately described merely as consisting of two phases. Three micromechanics model consisting of an inclusion embedded in a second inclusion phase



Three phases Model (Analytical):

$$C = C^m + \left(\left(V^{NP} + V^i\right)\left(C^i - C^m T\right)T^i + V^{NP}\left(C^{NP} - C^i\right)T\right)\left(V^m I + \left(V^{NP} + V^i\right)T^i\right)^{-1}$$

Use MD to extract the behavior of the interphase

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Challenge

- The thickness of the interphase is determined through the distribution of radial densities around the NP

- Combining MD and Multiscale tools (Analytical or Homogenization) to extract the mechanical properties of the interphase (Odegard et al., 2005; Choi et al.,2016)

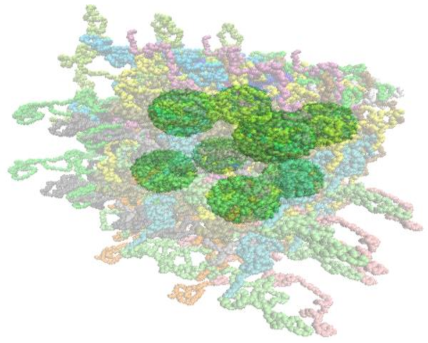
- Determination of properties of the interphases through MD still a main challenge

- Knowing the properties of the interphases facilitate the sensitivity analysis for mechanical properties of PNC by using analytical model or homogenization

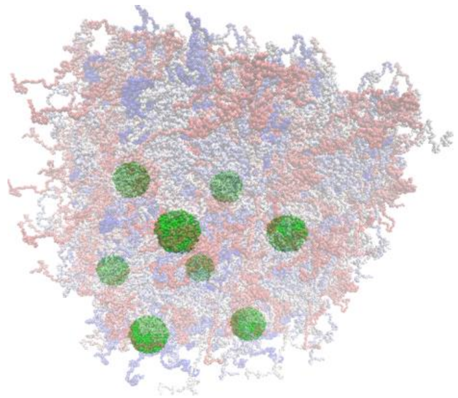
SUMMARY

- Characterization of Polymer/Nanoparticle Interphase
- Mechanical Properties of Atomistic PNCs
- Coupling between Atomistic and Continuum scale via Homogenization Approaches

Atomistic Model



PNC with 12 % Vf of Silica NP



PNC with 1.7 % Vf of Silica NP

PNC with 12 % Vf of NP					
NP/box	Nb of PB atoms	Nb of SI atoms	Nb of PB chains	NB of Si chains	Uncorrelated configuration
64	588800	196416	1472	64	10
PNC with 1.7 % Vf of NP					
NP/box	Nb of PB atoms	Nb of SI atoms	Nb of PB chains	NB of Si chains	Uncorrelated configuration
8	883200	24552	2208	8	10

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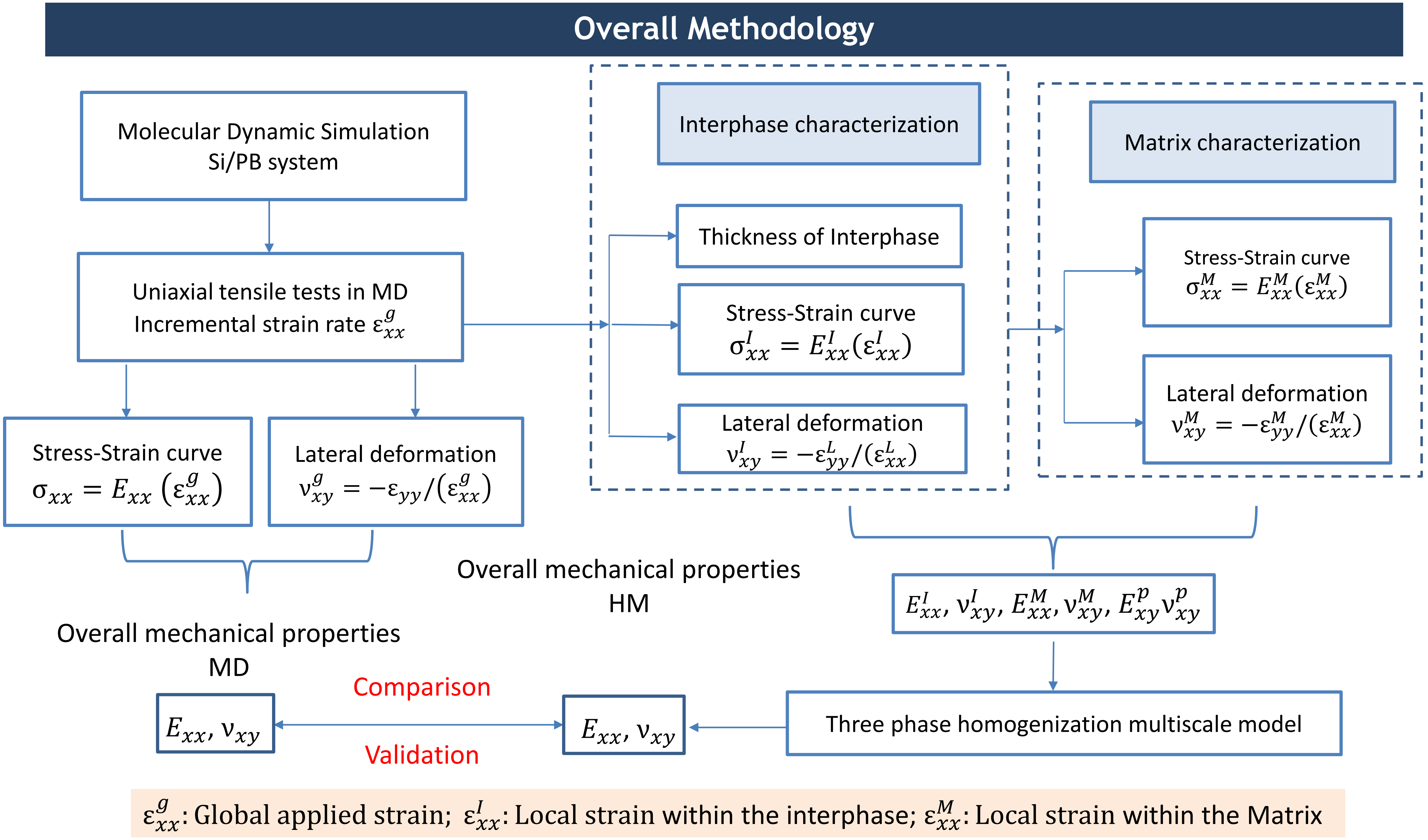
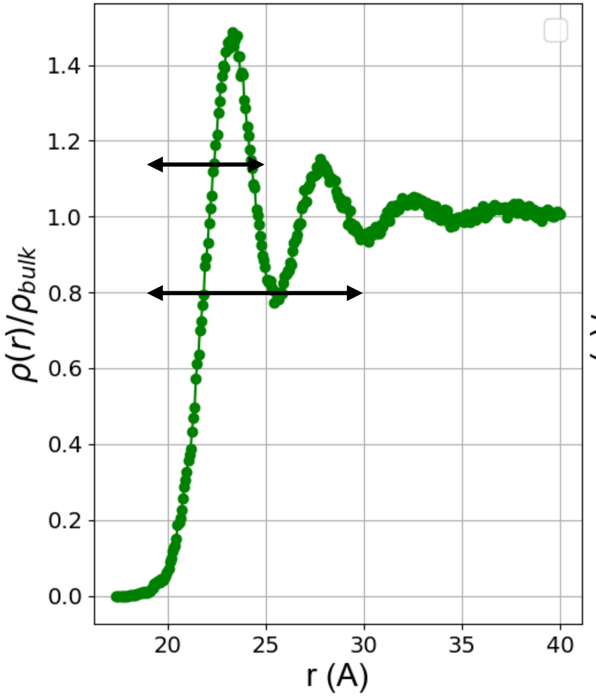


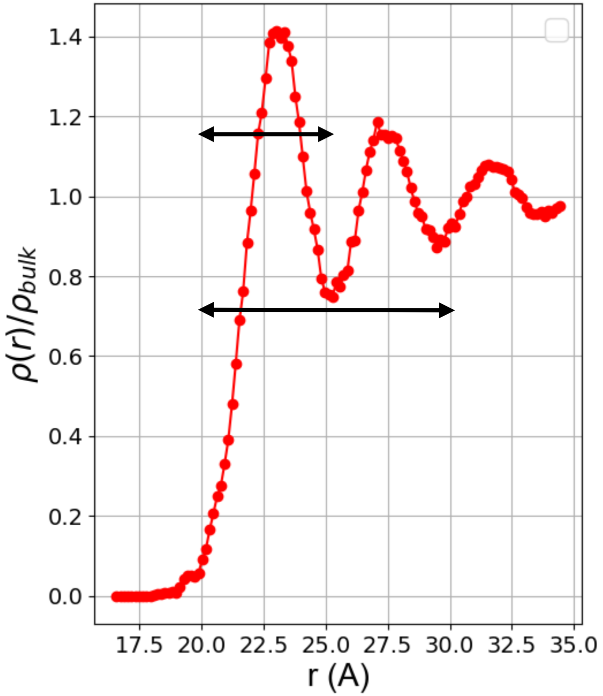
Overall Methodology
Molecular Dynamic Simulation
Si/PB system
Uniaxial tensile tests in MD
Incremental strain rate ε_{xx}^{g}
Stress-Strain curve
$\sigma_{xx} = E_{xx}\left(\varepsilon_{xx}^{g}\right)$
Lateral deformation
$\nu_{xy}^{g} = -\varepsilon_{yy}/(\varepsilon_{xx}^{g})$
Interphase characterization
Thickness of Interphase
Stress-Strain curve
$\sigma_{xx}^{I} = E_{xx}^{I}(\varepsilon_{xx}^{I})$
Lateral deformation
$\nu_{xy}^{I} = -\varepsilon_{yy}^{L}/(\varepsilon_{xx}^{L})$
Matrix characterization
Stress-Strain curve
$\sigma_{xx}^{M} = E_{xx}^{M}(\varepsilon_{xx}^{M})$
Lateral deformation
$\nu_{xy}^{M} = -\varepsilon_{yy}^{M}/(\varepsilon_{xx}^{M})$
Overall mechanical properties
HM
$E_{xx}^{I}, \nu_{xy}^{I}, E_{xx}^{M}, \nu_{xy}^{M}, E_{xy}^{p}\nu_{xy}^{p}$
Overall mechanical properties
MD
Comparison
E_{xx}, ν_{xy}
E_{xx}, ν_{xy}
Three phase homogenization multiscale model
Validation
ε_{xx}^{g}: Global applied strain; ε_{xx}^{I}: Local strain within the interphase; ε_{xx}^{M}: Local strain within the Matrix

Atomistic Molecular Simulations

- Several independent (uncorrelated) configurations of well-equilibrated atomistic PNCs, at high T (413 K)
- Atomistic model systems are cooled well below Tg, with a cooling rate of 10 K/ns down to 150 K (Effect of cooling rate). The experimental Tg of cis-1,4-PB is around 200K
- Uniaxially deformed with a constant strain rate of $\dot{\varepsilon} = 3\times10^{-6}\ fs^{-1}$
- Assume a well dispersed NP scenario, in which silica NPs are in a simple cubic like arrangement within the polymer matrix, i.e there is no any aggregation of the NPs
- The overall applied deformation is up to 0.6, but we will focus more on the linear regime.

- Probing the thick of the interphase polymer in Nanocomposite by the distribution of density profile at equilibration





Interfacial atomic density profiles for nanocomposites of 100-mer consisting of 1.7 % and 12 % volume percentage of NP

R1 : zone of interphase 1 with thick 6 A from the outer surface of NP

R2 : zone of interphase 2 with thick 11 A from the outer surface of NP

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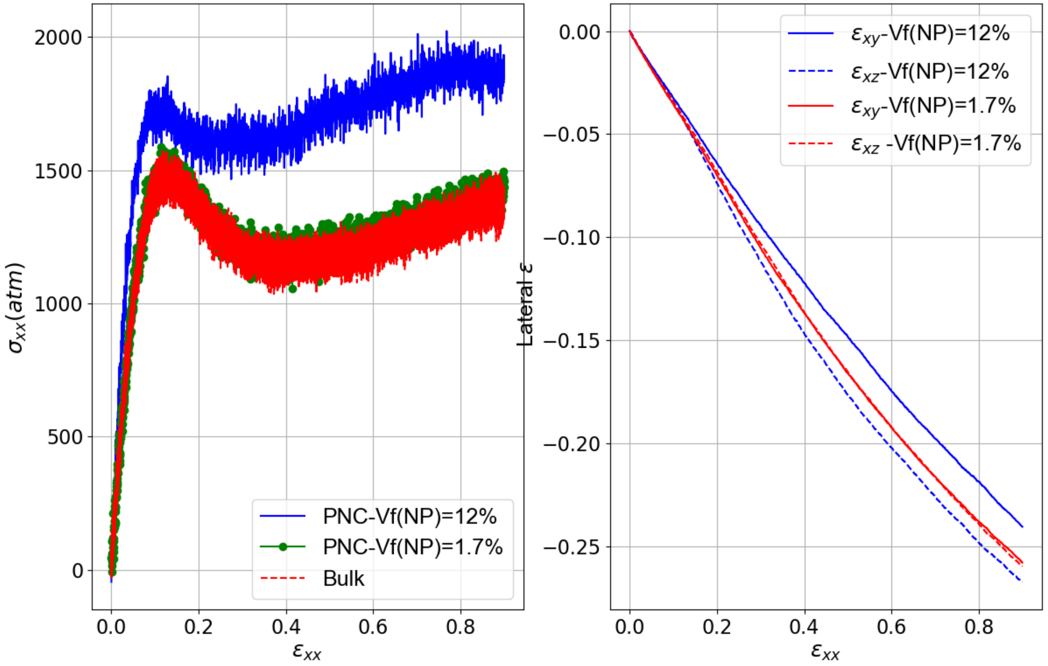
- # Overall properties of the PNC

Young’s modulus and Poisson’s ratio are measured from the simple tension test by applying incremental strain rate to the atomistic structures by means of a modified NPT ensemble in MD simulation



- An elastic regime exists where the stress is linear depending by the strain according to Young Modulus E_{xx} = 2.238 Gpa (NC with 12% of NP) (Poisson's ratio is around 0.33)

- For low volume percentage of NP (1.7%), the mechanical properties of the NC are similar to the pure homogenous PB material.

- For the bulk system (refer to homogeneous polymers involving a continuous single phase domain), the effective Young Modulus is E= 1.19 Gpa and a Poisson's ratio 0.345.

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Mechanical Properties of Atomistic PNCs

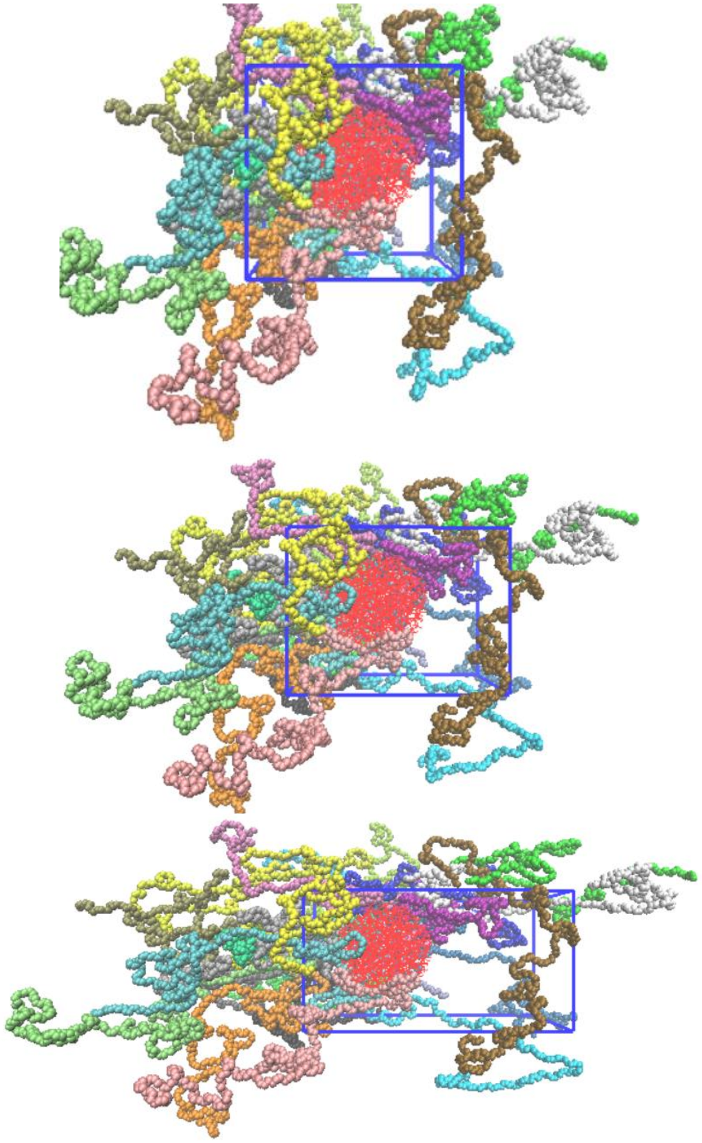
- **Applied incremental strain rate on the cubic box**

- Uniaxially deformed the unit box with a constant strain rate of $\dot{\varepsilon} = 3\times10^{-6}\ fs^{-1}$

- The uniaxial deformation of the box, as implemented in Lammps, respects the boundary condition along the axis of deformation

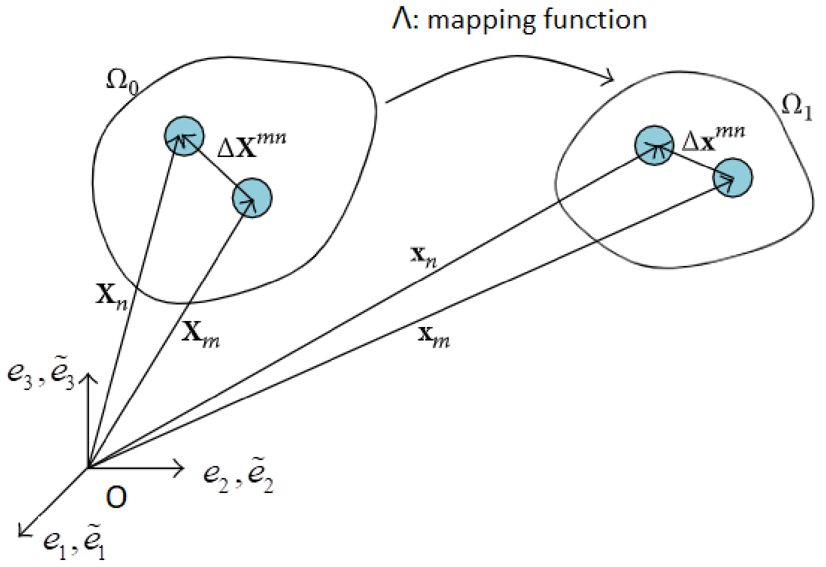
- In the deformation process, an affine strain field is produced in the bulk sample. However, in PNCs, the presence of highly stiff NPs leads to a non-affine strain field in the sample

- NPs practically do not experience any strain, but their presence alters the local strain within the polymer in the vicinity of the NP



• Spatial distribution of the effective rigidity matrix in PN

- Atom m is located at the position X^m in the reference configuration Ω_0 and position x^m in the current configuration Ω



$$\Delta\mathbf{x}^{mn} = \mathbf{x}^n - \mathbf{x}^m$$

$$\Delta\mathbf{X}^{mn} = \mathbf{X}^n - \mathbf{X}^m$$

$$\Delta\mathbf{x}^{mn} = \mathbf{F}^m \Delta\mathbf{X}^{mn}$$

- The deformation gradient $\mathbf{F}^m$ of atom m is related to its neighboring atoms
- $\mathbf{F}^m$ of atom m cannot generally be determined by a single atom n
- $\mathbf{F}^m$ can be determined through the squares error minimization function W^m shown in the following equation :

$$W^m = \sum_{n=1}^{N} \left(\Delta\mathbf{x}^{mn} - \mathbf{F}^m \Delta\mathbf{X}^{mn}\right)^T \left(\Delta\mathbf{x}^{mn} - \mathbf{F}^m \Delta\mathbf{X}^{mn}\right)$$

- When the minimization function W^m reaches the minimum, the parameters F^m are the optimal components of the optimal deformation gradient matrix

The Lagrangian Green strain tensor ε

$$\boldsymbol{\varepsilon} = \frac{1}{2}\left(\mathbf{F}\,\mathbf{F}^{\mathrm{T}} - \mathbf{I}\right)$$

ε_{xx}^{I}: Local strain within the interphase

ε_{xx}^{M}: Local strain within the Matrix

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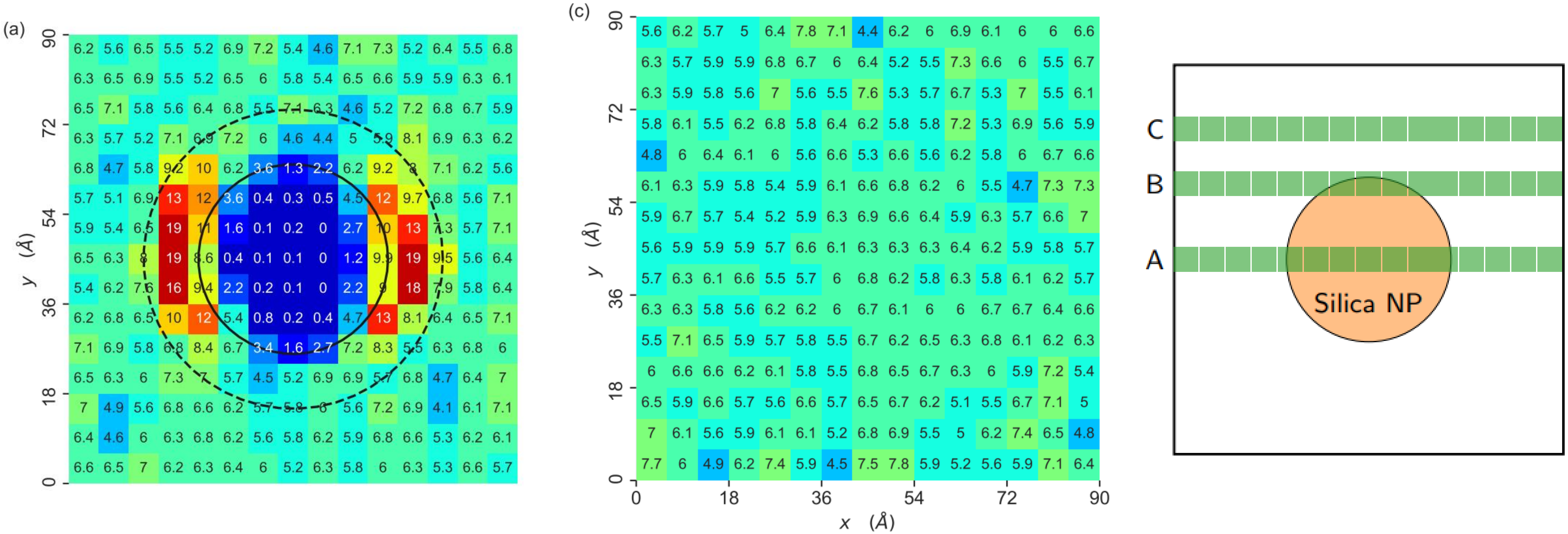
• Spatial distribution of the effective rigidity matrix in PNCs

- The distribution of local strain between atomic scale simulations and the continuum level must be provided
- Strain tensor will be calculated based on the strain gradient deformation tensor and the minimization function methodology



Affine deformation AFD that exactly matches the box deformation in the case of matrix polymer
While for the case of heterogeneous NC, this will not be the case as we can have observed

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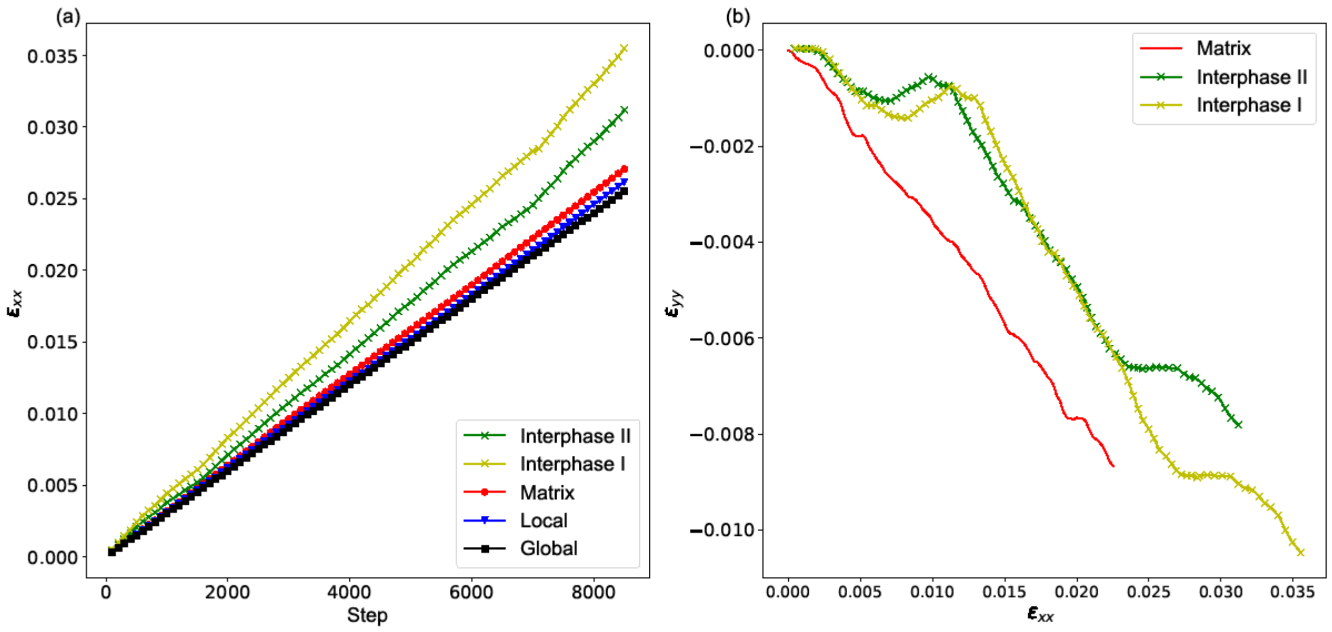
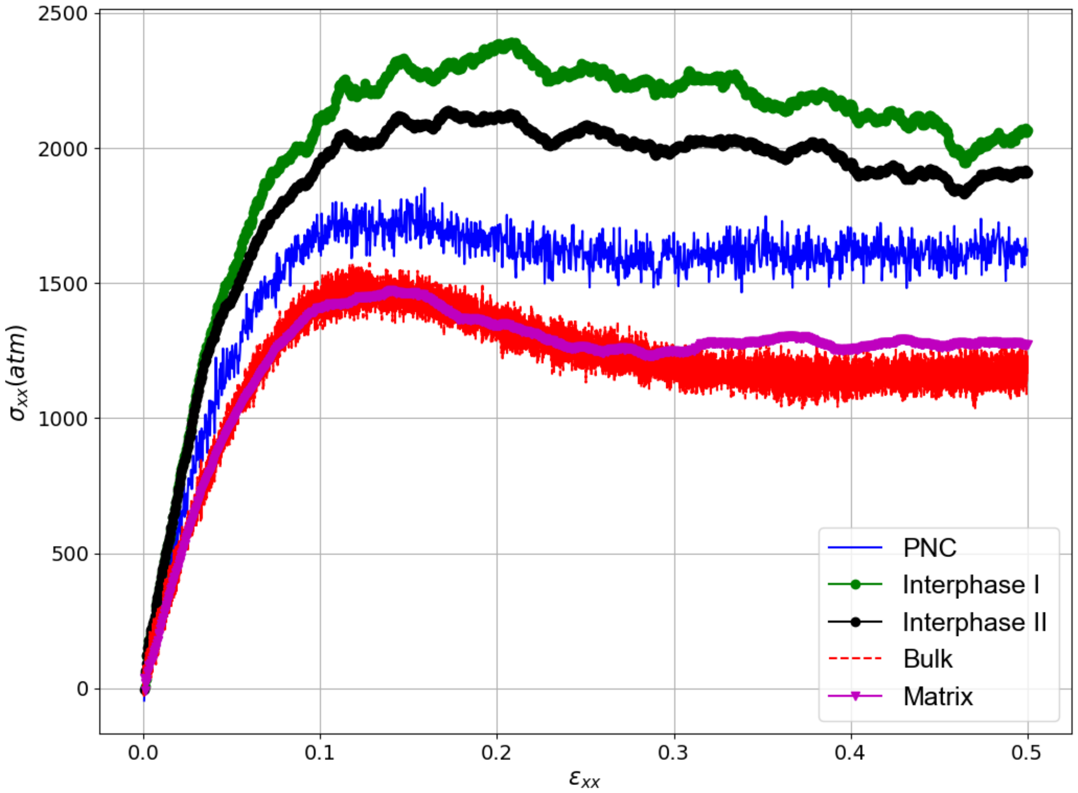
- **Spatial distribution of the effective rigidity matrix in PNCs**

- The local strain and stress will be averaged in a thin sphere with thickness corresponding to the Interface region I and II



Average local stress is to close from the global applied strain and the relative error does not exceed 6% after 8000 steps (limited to the elastic region)



Stress–strain (local) curves for Interfaces, Bulk region and pure homogenous PB (polybutadiene)

$E^I_{xx}, \nu^I_{xy}, E^M_{xx}, \nu^M_{xy}$

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- **Through Molecular dynamic simulation**

Effective Young modulus and poison ration for Interface I, II and Bulk calculated based on axial strain deformation on NPT ensemble

Applied Strain	Interphase I	Interphase II	Polymer
ε_{xx}	$E_{xx} = 3.54\,GPa$	$E_{xx} = 3.324\,GPa$	$E_{xx} = 1.168\,GPa$
	$\nu_{xy} = 0.326$	$\nu_{xy} = 0.316$	$\nu_{xy} = 0.346$
	$\nu_{xz} = 0.328$	$\nu_{xz} = 0.317$	$\nu_{xz} = 0.349$

• Multiscale modeling approach towards Cauchy medium

- Homogenization of heterogeneous materials towards Cauchy type effective continua, for which only the first displacement gradient is of importance
- The average of microscopic energy evaluated over the unit cell is equal to the energy of the effective continuum at the mesoscopic level

$$W_M(\mathbf{E}) = \frac{1}{2}\mathbf{E} : C^{hom} : \mathbf{E} = \langle w_\mu(\boldsymbol{\varepsilon}) \rangle_Y = \left\langle \frac{1}{2}\boldsymbol{\varepsilon}(\mathbf{y}) : C(\mathbf{y}) : \boldsymbol{\varepsilon}(\mathbf{y}) \right\rangle_Y$$

- The objective is to calculate the global rigidity C^{hom} from the rigidities of constituent C(y) after applied boundary condition
- The microscopic deformation can be decomposed into their homogeneous and fluctuating parts by introducing the macroscopic deformation

$$\boldsymbol{\varepsilon}(\mathbf{y}) = \boldsymbol{\varepsilon}^{hom}(\mathbf{x}) + \tilde{\boldsymbol{\varepsilon}}(\mathbf{y}),$$

$$\boldsymbol{\varepsilon}^{hom}(\mathbf{x}) := \mathbf{u}^{hom}(\mathbf{y}) \otimes^S \nabla_y = \mathbf{E}$$

- $\tilde{\boldsymbol{\varepsilon}}(\mathbf{y})$ represents the fluctuating part of the microscopic strain, at the micro-scale materials are considered elastic and isotropic

- The weak formulation of equilibrium is introduced to get the following formal homogenized problem, considering the decomposition of the total microscopic deformation

$$\forall \mathbf{v} \in (Y), \int_Y \mathrm{div}\left(C(\mathbf{y}) : \boldsymbol{\varepsilon}(\mathbf{u})\right) : (\mathbf{v}) dV_y = 0$$

Solving this variational formulation, the microscopic deformation will obtained

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• Multiscale modeling approach

•The microscopic stress at a position **y** is obtained using the relation:

$$\begin{pmatrix}\sigma_{11}\\ \sigma_{22}\\ \sigma_{12}\end{pmatrix} = \begin{pmatrix}\lambda+2\eta & \lambda & 0\\ \lambda & \lambda+2\eta & 0\\ 0 & 0 & 2\eta\end{pmatrix}\begin{pmatrix}\tilde{\varepsilon}_{11}+E_{11}\\ \tilde{\varepsilon}_{22}+E_{22}\\ \tilde{\varepsilon}_{12}+E_{12}\end{pmatrix}$$

$$\boldsymbol{\varepsilon}(\mathbf{y}) = \boldsymbol{\varepsilon}^{\text{hom}}(\mathbf{x}) + \tilde{\boldsymbol{\varepsilon}}(\mathbf{y}),$$
$$\boldsymbol{\varepsilon}^{\text{hom}}(\mathbf{x}) := \mathbf{u}^{\text{hom}}(\mathbf{y}) \otimes^{S} \nabla_{y} = \mathbf{E}$$

λ and η are the Lame coefficient
are function of Young modulus and poison ratio

• The macroscopic stress leads to the calculation of the effective rigidity matrix

$$\begin{pmatrix}\sigma_{11}\\ \sigma_{22}\\ \sigma_{12}\end{pmatrix}^{macro} = \begin{pmatrix}c_{11} & c_{12} & c_{13}\\ c_{12} & c_{22} & c_{23}\\ c_{13} & c_{23} & c_{33}\end{pmatrix}\begin{pmatrix}E_{11}\\ E_{22}\\ E_{12}\end{pmatrix} = \left\langle \begin{pmatrix}\sigma_{11}\\ \sigma_{22}\\ \sigma_{12}\end{pmatrix}^{micro} \right\rangle_{Y}$$

• Applying E11=1, E22=E12=0 leads to the calculation of the first column of C hom

•Applying E11=0, E22=1, E12=0 leads to the calculation of the second column of C hom

•Applying E11=0, E22=0, E12=1 leads to the calculation of the third column of C hom

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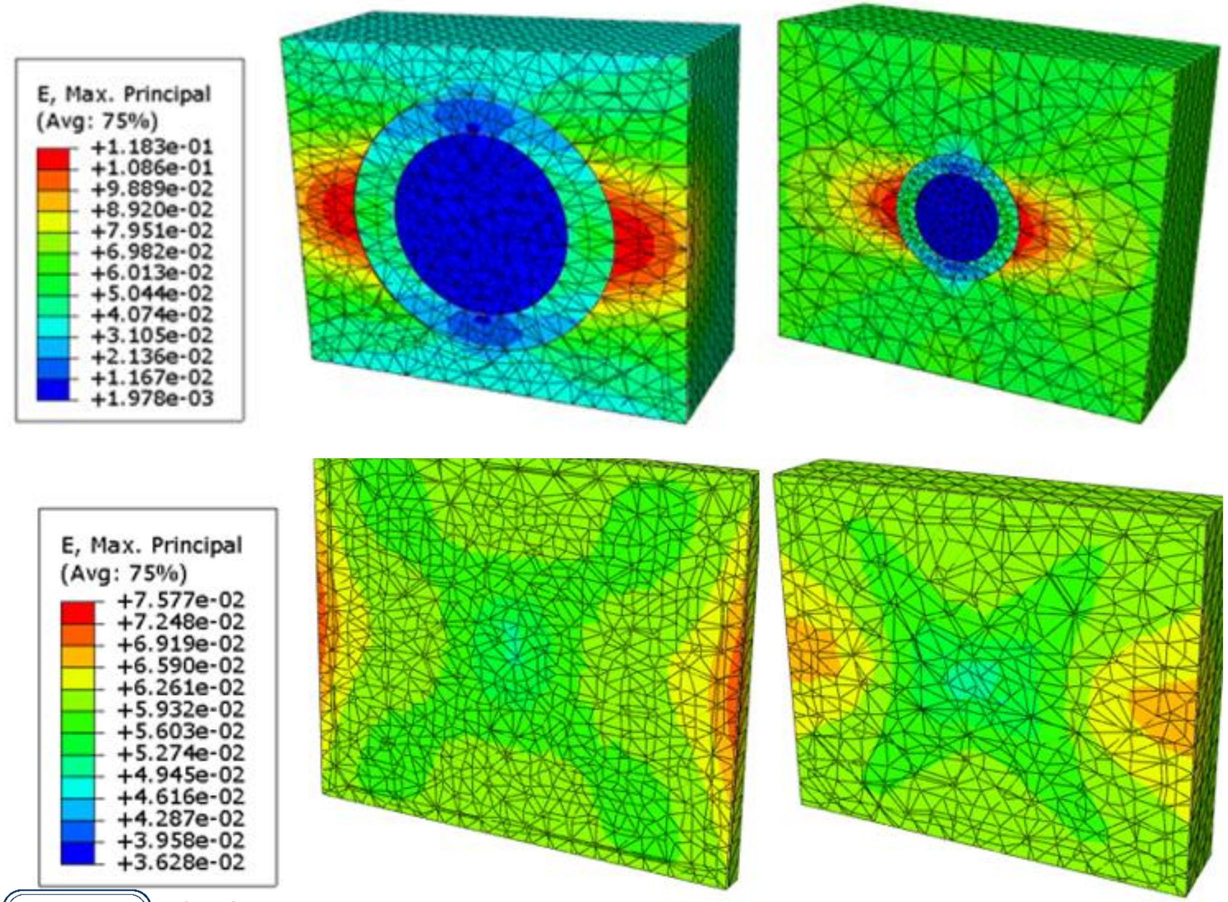
• Multiscale modeling approach

• Distribution of local strain through homogenization



- The non-affine distribution of the deformation within the material when applying external normal deformation is clearly observed
- Higher deformation occurs at the interphases which is in good agreement with the results from MD
- The distribution of local strain in matrix polymer match the applied one and represent good agreement to the distribution of strain obtained by MD (Affine deformation in homogeneous medium)

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- **Coupling between Atomistic and Continuum scale via Homogenization Approaches**

Mechanical properties	Nc (12%)				Nc (1.7%)			
	Homogenization Method			MD	Homogenization Method			MD
	Interphase I	Interphase II	Without Interphase		Interphase I	Interphase II	Without Interphase	
E_{xx}(MPa)	2.14	2.208	1.938	2.238	1.141	1.173	1.05	1.19
Poison ratio	0.328	0.336	0.283	0.33	0.341	0.35	0.304	0.345

Good agreement for NP based composite, with a maximum relative error of 5 %.

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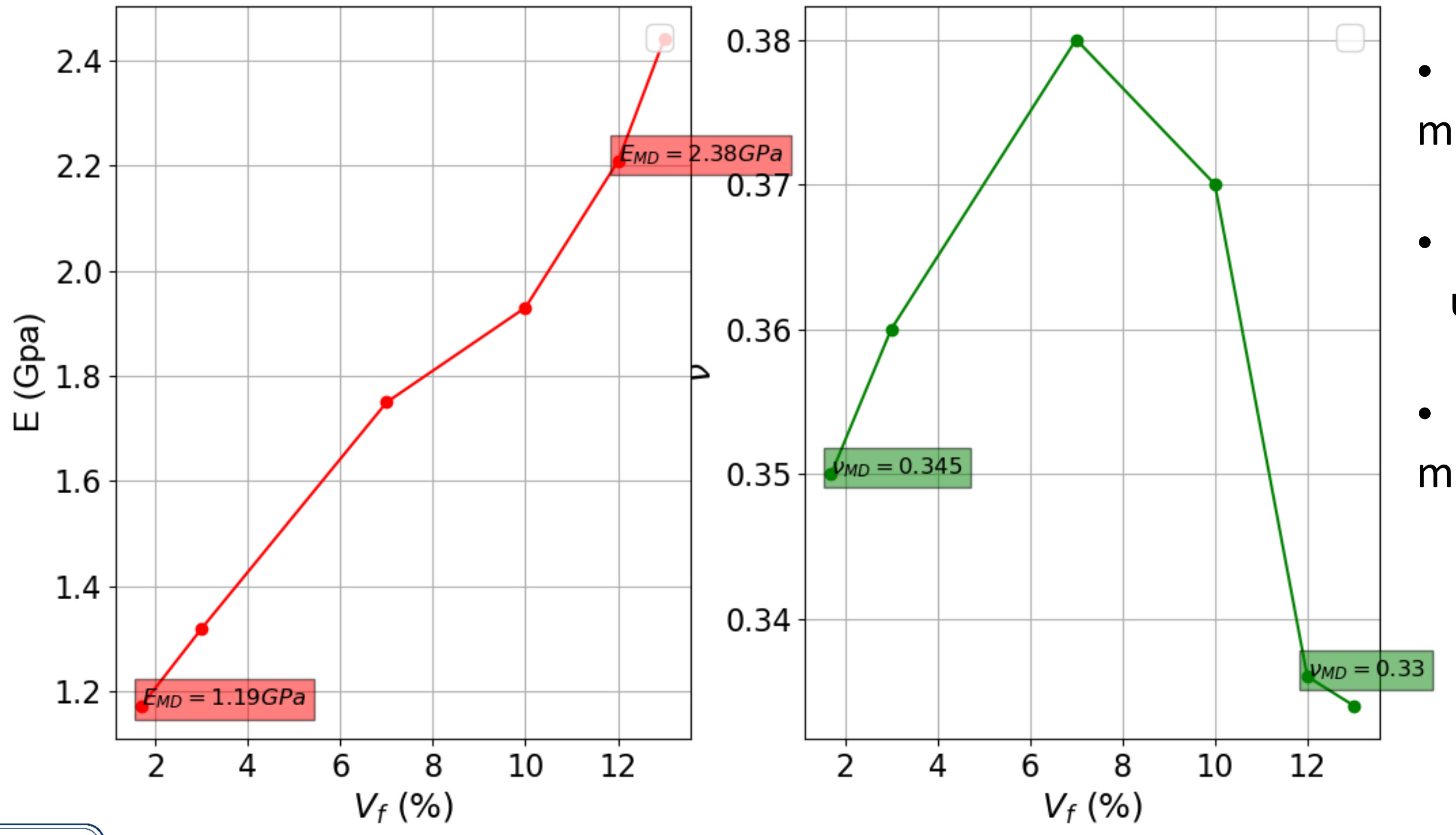
- **Mechanical properties of different PNC system**

The main advantage of the newly parametrized effective medium continuum model is to allow the prediction of the mechanical properties of NC with different volume fraction of NP having the same size



- Increasing the volume percentage, the Young modulus increase in nonlinear manner
- The poison ratio increase when increasing V_f up to certain limit after which it start to decrease
- Increasing Vf leads to decrease the region of pure matrix and then decreasing the lateral deformation

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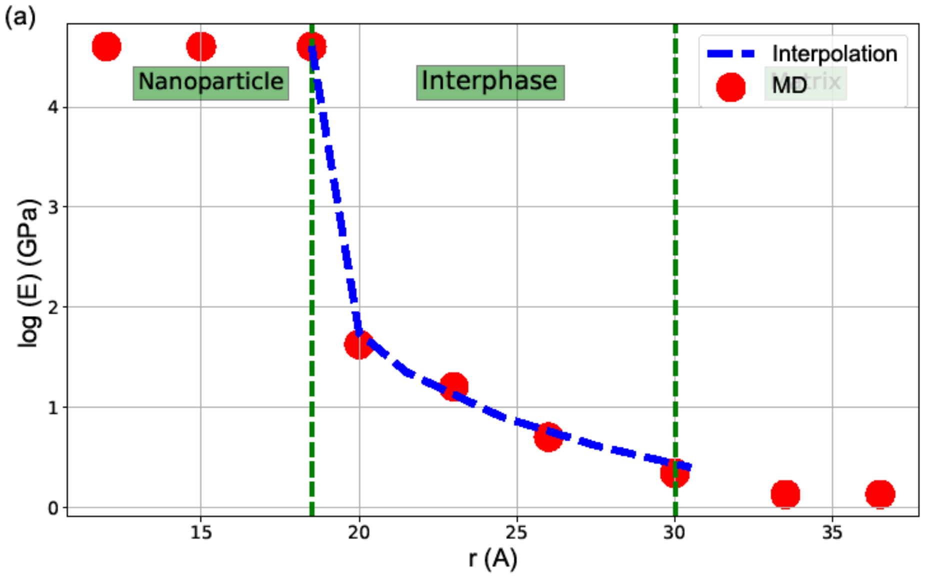
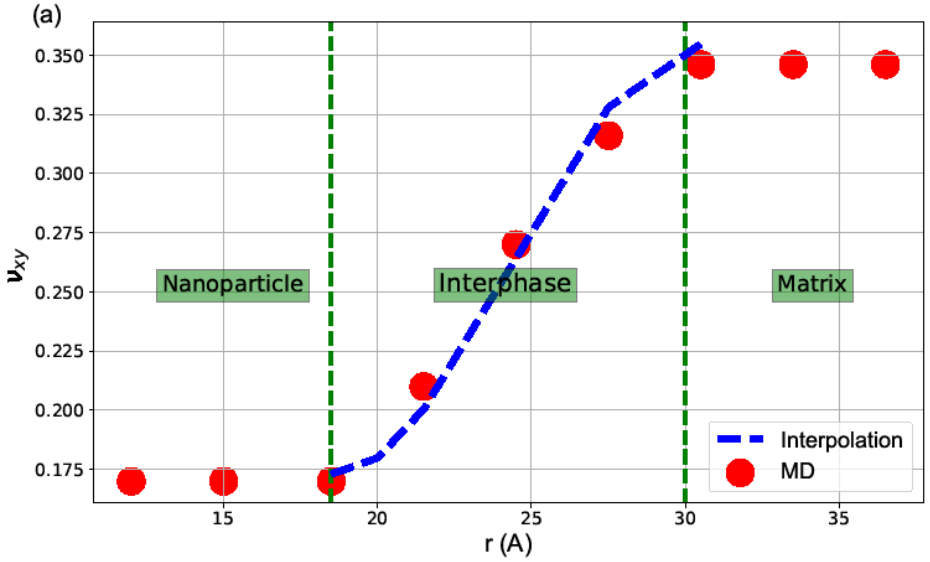
Characterization of Interphase by generalized medium

- **Spatial distribution of the Mechanical properties of Interphases**

Variation of the Young's modulus and Poison within the RVE as a function of radius from the center of NP.
Red points correspond to the results from MD





- Gradient of mechanical properties is observed
- Cauchy type medium is insufficient to describe the mechanical behavior of the interphase

$$E(r) = E_0 exp^{-\alpha(x-r_0)^{\beta}}$$

$$\nu(r) = ar^3 + br^2 + cr + d$$

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- **Spatial distribution of the Mechanical properties of Interphases**

Effective Young modulus E (Gpa) and shear modulus (Gpa) from different models

	PB/Si				PEO/Si			
	12 %		1.7%		16 %		2%	
	E	G	E	G	E	G	E	G
MD	2.24	1.1	1.19	0.62	5.82	2.86	3.85	1.37
HM	2.208	0.82	1.17	0.52	5.86	2.14	3.49	1.21
MT	1.51	0.68	1.1	0.42	4.82	2.28	3.26	0.92
3 PM	2.14	0.94	1.26	0.5	5.54	2.51	3.79	1.16
E 3 PM	2.22	0.97	1.21	0.53	5.61	2.62	3.71	1.19

3 PM: Three phases medium with constant properties of interphase
E 3 PM : Three phases medium with realistic model of interphase

$$\mathbf{C}^I = \frac{1}{(r_I - r_{NP})} \int_{r_{NP}}^{r_I} \mathbf{C}^I(r)dr$$

Characterization of Interphase by generalized medium

- The extended Cauchy–Born rule will take into consideration the second-order of deformation gradient

$$\Delta\mathbf{x}^{mn} = \mathbf{F}_m \Delta\mathbf{X}^{mn} + \frac{1}{2}\mathbf{G}_m\left(\Delta\mathbf{X}^{mn} \otimes \Delta\mathbf{X}^{mn}\right)$$

- The optimal local deformation gradient $\mathbf{F}_m$ ($\mathbf{x}$) and the second order deformation gradient $\mathbf{G}_m$, which can make the squares error W_m shown in the following equation minimized

$$W_m = \sum_{n=1}^{N}\left(\Delta\mathbf{x}^{mn} - \mathbf{F}_m(\mathbf{x})\Delta\mathbf{X}^{mn} - \frac{1}{2}\mathbf{G}_m\left(\Delta\mathbf{X}^{mn} \otimes \Delta\mathbf{X}^{mn}\right)\right)^T\left(\Delta\mathbf{x}^{mn} - \mathbf{F}_m(\mathbf{x})\Delta\mathbf{X}^{mn} - \frac{1}{2}\mathbf{G}_m\left(\Delta\mathbf{X}^{mn} \otimes \Delta\mathbf{X}^{mn}\right)\right)$$

where N is the number of neighboring atoms of maximum distance r cutoff.

- The Lagrangian Green strain tensor **E** and the gradient of deformation **K** are obtained through

$$\mathbf{E}_m = \frac{1}{2}\left(\mathbf{F}_m \mathbf{F}_m^{\mathrm{T}} - \mathbf{I}\right), \qquad \mathbf{K}_m = \mathbf{F}_m^{\mathrm{T}}\left(\mathbf{F}_m \otimes \nabla\right)$$

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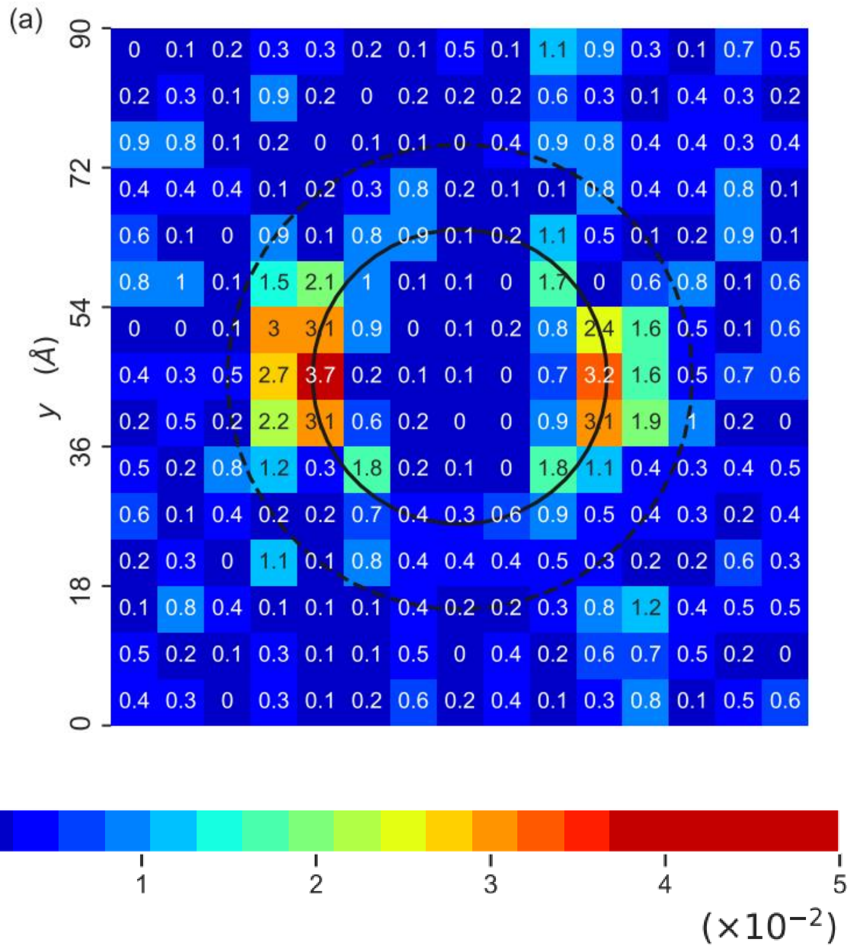
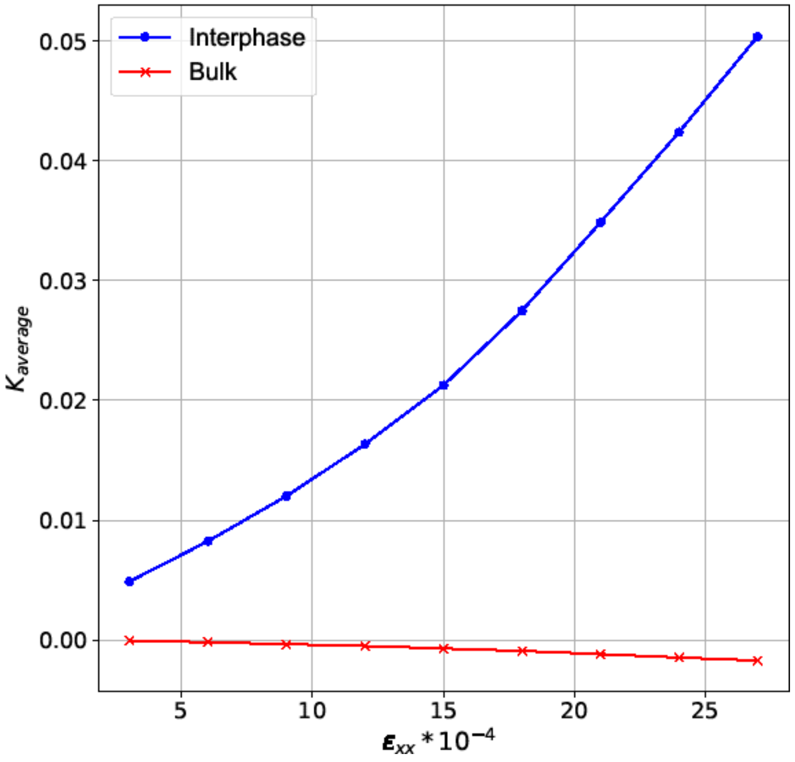
Characterization of Interphase by generalized medium

Distribution of gradient of deformation within PNC system



1. At the interphase, the gradient of deformation is remarkable
2. The gradient of deformation within the matrix is negligible
3. The interphase cannot be described by simple Cauchy medium



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Linking MD simulations to strain gradient homogenized

1. The hyperstress tensors for each atom m are calculated based on the averaging relations:

$$S_{ijk}^{m} = \frac{1}{\Omega^{m}} \left(\frac{1}{2} m^{m} v_{i}^{m} v_{j}^{m} r_{m,\beta}^{k} + \sum_{\beta=1,n} r_{m,\beta}^{j} \, f_{m,\beta}^{i} r_{m,\beta}^{k} \right)$$

2. The Cauchy and strain gradient moduli are obtained for a domain Ω by minimization the average quadratic norm of the difference between the energy

$$Min : W_{\Omega}(\mathbf{B}_{\Omega}^{hom}, \mathbf{C}_{\Omega}^{hom}, \mathbf{D}_{\Omega}^{hom}) = \left(\sum_{n=1}^{N_{load}} \left\| \mathbf{W}^{(m,MD)} - \mathbf{W}^{\mu}(\mathbf{B}_{\Omega}^{hom}, \mathbf{C}_{\Omega}^{hom}, \mathbf{D}_{\Omega}^{hom}) \right\|^{2} \right)^{\frac{1}{2}},$$

$$W^{(m,MD)} = \frac{1}{2} \sum_{m=1}^{N_{atoms}} \left(\sigma_{ij}^{m} \mathbf{E}_{\mathbf{ij}}^{\mathbf{m}} + S_{ijk}^{m} \mathbf{K}_{\mathbf{ijk}}^{\mathbf{m}} \right)$$

$$W^{\mu} = \frac{1}{2} \left(\mathbf{E}^{T} \mathbf{C}^{hom} \mathbf{E} + \mathbf{K}^{T} \mathbf{D}^{hom} \mathbf{K} \right)$$

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