Method Article

A methodology for determining the local mechanical properties of model atomistic glassy polymeric nanostructured materials

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\textbf{ABSTRACT}

We propose a methodology for calculating the distribution of the mechanical properties in model atomistic polymer-based nanostructured systems. The use of atomistic simulations is key in unravelling the fundamental mechanical behavior of composite materials. Most simulations involving the mechanical properties of polymer nanocomposites (PNCs) concern their global (average) properties, which are typically extracted by applying macroscopic strain on the boundaries of the simulation box and calculating the total (global) stress by invoking the Virial formalism over all atoms within the simulation box; thus, extracting the pertinent mechanical properties from the corresponding stress-strain relation.

However, in order to probe the distribution of mechanical properties within heterogeneous multi-component polymer-based systems, a detailed computation of stress and strain fields within specific sub-domains is necessary. For example, it is well known for multi-component nanostructured systems, such as PNCs, that the mechanical behavior of the polymer/nanofiller interphases, or interfaces, is crucial for determining the global mechanical properties of the composite materials. Here we propose a new methodology to probe the distribution of mechanical properties by directly computing the (local) stress and strain at the atomic level, and averaging over user-defined subdomains. The workflow of our computational method possesses the following features:

- Calculating the stress and strain per atom (or per particle) for nanostructured microscopic (here atomistic) model configurations, under an imposed applied deformation.
- Averaging the local, per-atom defined, stress and strain on user-defined subdomains within the nanostructured model system.
- Predicting the mechanical properties within the specific subdomains, focusing on polymer/solid interphases.

\textbf{DOI of original article:} 10.1016/j.cma.2022.114905
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Specifications Table

| Subject Area: | Materials Science |
|---------------|-------------------|
| More specific subject area: | Nanostructured materials, Polymer nanocomposites |
| Method name: | Method for computing the distribution of mechanical properties in atomistic nanostructured model systems (NANOMEC) |
| Name and reference of original method: | H. Reda, A.Chazirakis, A. Behbahani, N. Savva, V. Harmandaris, “Mechanical properties of glassy polymer nanocomposites via atomistic and continuum models: The role of interphases”, Computer Methods in Applied Mechanics and Engineering 395, 114905 (2022). |
| Resource availability: | https://github.com/SimEA-ERA/NANOMEC.git |

Method details

A main challenge in the computational studies of multi-component nanostructured materials involves the prediction of their mechanical properties directly from their molecular structure, which are inherently heterogeneous. This is particularly important for hybrid systems, such as polymer nanocomposites (PNCs). In recent years PNCs have been extensively employed in numerous technological innovations across a broad spectrum of applications, coming from, e.g., mechanical, aerospace, electrical, and (bio)chemical engineering [1–4], due to their exceptional (mechanical, chemical, electronic, etc.) properties, compared to the corresponding bulk homogeneous materials. For this reason, research on the theoretical and computational modeling of mechanical properties of polymer-based nanostructured systems, and especially of PNCs with nanoscale reinforcement fillers, has intensified during the last few decades [5,6].

Nanostructured materials exhibit unique design capabilities that meet the needs in industry especially for the lightweight design of advanced equipment, which offer brilliant advantages in creating functional nanostructured materials with tunable mechanical properties. Therefore, the mechanical design of polymer-based nanostructured systems is an important subject in polymer science and technology. The reinforcing effect of the nanofiller in PNCs is attributed to several factors, such as properties of the polymer matrix, type of nanofiller, volume concentration of polymer and filler, particle size, particle aspect ratio, particle orientation and particle distribution [5]. Various types of fillers, such as nanoparticles (NP) [5,6], carbon nanotubes [7] and graphene [8], have been used for obtaining nanocomposites with different polymers. In all cases, it is nowadays recognized that the mechanical properties of PNC materials strongly depend on the behavior of the polymer/nanofiller interfacial region, even for low nanofiller loadings [9].

From a theoretical standpoint, several micromechanical models have been proposed in the literature for predicting the effective properties of nanocomposites [10–12]. These models are typically based on classical Eshebly tensors [13], which are derived after selecting an infinite representative volume element (RVE), and do not consider any interphase effects between fillers and matrix polymer. Such an example is the Mori-Tanaka model, whereby the filler and the polymer matrix are assumed to be perfectly bonded in a continuous manner [12]. Another example is a three-phase composite model, whereby the matrix medium encapsulates a filler embedded within a second filler phase (the second filler phase represents the interphase region) [14]. These modeling efforts have demonstrated the need for the development a new micromechanical model that is able to predict the mechanical
properties of a PNC. This need is further highlighted because, in addition to the bulk and NP properties, the interfacial region also strongly influences the effective properties of the material [15,16]. For that reason, accurately describing the overall PNC behavior with some micromechanical model requires that the interphase region and the nature of the polymer/filler interactions are also properly accounted for.

To overcome the above limitations of the theoretical models, and, at the same time, provide a detailed investigation of the mechanical behavior at the atomic scale, detailed atomistic simulations are used. Their outcomes are then analyzed to examine the properties of a simulated model system and determine its mechanical properties by investigating the resulting stress and strain fields within the domain of interest. However, such inherently heterogeneous stress-strain data have been proven difficult to characterize at the atomic scale in a systematic and consistent manner, as well as in terms of computing costs. While a lot of effort has been invested in establishing expressions for the stress at the atomic level [17], mainly via the atomic Virial formalism, the proper definition of the strain on the atomic-scale, based on the deformation gradient, has received far less attention [18–20].

Due to the inhomogeneities in the density and polymer chain conformations in PNCs, the accurate prediction of their effective mechanical behavior, directly via the distribution of local stress/strain fields, is a major challenge. Moreover, if such data are obtained at the local-atomic level, they can be further used to derive accurate micromechanical models that consider explicitly the polymer/nanofiller interphase. To address such challenges and requirements, we present the method termed “NANOMEC”, which allows us to provide a direct estimation of the local mechanical properties at the atomic level of any, arbitrarily chosen, subdomain within heterogeneous polymer-based nanostructured model systems. As an application, the methodology is used for determining the distribution of the mechanical properties in atomistic model PNCs, focusing on the polymer/nanofiller interfacial regions. The method is based on non-equilibrium atomistic molecular dynamics (MD) simulation and advanced optimization algorithms, without any input from continuum models. At the same time, our methodology does not rely on experimental data.

In this paper, we focus more on the technical description of the proposed computational methodology. For more details about the theoretical background and results about its application to a specific PNC system, we refer the reader to the recent original work [21].

**Methodology for the calculation of local mechanical properties**

Here we describe in detail the proposed method for calculating the distribution of mechanical properties in atomistic model systems, under an external applied loading. Although the working principle of NANOMEC can be easily generalized to any multi-component nanostructured system, in the following we consider for simplicity PNCs with well-dispersed NPs as fillers. NANOMEC involves detailed non-equilibrium atomistic simulations and advanced optimization algorithms as shown in the associated workflow, presented in Fig. 1.

The whole methodology can be summarized as follows:

- **Initialization**: Start from realistic model configurations obtained via long equilibrium atomistic simulations;
- **Stage 1**: Assuming a given strain rate, impose deformation in the equilibrium configurations up to a specific strain $\varepsilon$;
- **Stage 2**: Analyze the deformed configurations to compute the stress distribution in the model systems by calculating the stress per atom;
- **Stage 3**: Analyze the deformed configurations to compute the strain distribution in the model systems by calculating the strain per atom;
- **Stage 4**: For a specific domain decomposition scheme, compute the average stress and strain within the user-defined subdomains;
- **Stage 5**: Perform stages 1-4 iteratively for various deformations and values of strain $\varepsilon$ as well. Compute the mechanical properties within specific sub-domains of interest, via the local stress-strain relations.
Fig. 1. Flowchart for the derivation of elastic constitutive law within a user-defined subdomain $\Omega$. Input includes the atomistic model (force field) and the time step for integrating the equations of motion. The total running time $t_{\text{max}}$ determines the end of the process. The total strain is given by $\epsilon_t = \hat{\varepsilon} \times t_{\text{max}}$. $\sigma^\alpha$, $\epsilon^\alpha$ represent the atomic (defined for each atom) stress and strain of atom $\alpha$ while $\sigma^\Omega$, $\epsilon^\Omega$ denote the average stress and strain over the subdomain $\Omega$. $C^\Omega$ represents the effective rigidity tensor in $\Omega$, which can be determined by extracting the mechanical properties (e.g., Young’s modulus and the Poisson’s ratio) from the stress vs strain plot. $N_{\text{atoms}}$ are the number of atoms (or particles) within $\Omega$, whereas the indices $i, j, k, l$ represent indices in the Cartesian coordinate system ($x, y, z$).

In the following, we briefly discuss the various stages of the proposed hierarchical simulation framework for the computation of local mechanical properties. Note, that the method can be applied for any type of imposed applied deformation. Here, for simplicity, we present it for uniaxial deformation along the $x$ direction.

Initialization: Model configurations at equilibrium

NANOMEC starts assuming an available set of atomistic model configurations (i.e., Cartesian coordinates of all atoms within the simulation domain) of the heterogeneous nanostructured system under study. Such configurations can be obtained, for example, via detailed atomistic MD or Monte
Carlo simulations. We also assume a specific atomistic model (force field) describing in all-atom detail the underlying physical system. Last, for the applications considered here, we apply periodic boundary conditions (PBCs) in all directions. However, it is straightforward to extend the methods for systems with different type of boundary conditions.

Assuming a set of equilibrated atomistic configurations of model polymeric nanostructured systems at high temperature, well above the glass transition temperature, \( T_g \), we first apply a cooling towards the glassy regime \( (T<T_g) \). Then we perform short MD runs of the order of several ns, to allow for small-scale relaxation of the glassy model systems.

Stage 1: Deformation of model systems

Starting from the equilibrium configurations of the glassy systems, a non-equilibrium MD model was set up by applying a deformation of constant strain rate as boundary condition followed by a single molecular dynamic step. These deformation steps are performed with the Nose–Hoover thermostat and Parinello-Rahman barostat. Here, for these simulations we have used the open source LAMMPS software.

In the case of single-component amorphous, albeit relatively homogeneous, systems, such a deformation process results in an (almost) affine strain field, as expected. Thus, the deformation of atoms follows that of the box, resulting into a rather uniform distribution of strain within the bulk system. Indeed, this has been verified for bulk polymers, as it is seen below.

However, due to the sharp contrast in the rigidity of the polymer matrix and the, usually more rigid, NPs, with the NPs experiencing negligible strain, the distribution of the local strain field within the PNC becomes non-affine. In this manner, changes in the local strain field become more pronounced in the vicinity of the NPs. We should also note that, after each box deformation step, the atom positions are remapped to the new box in accordance with the PBCs along the axis of deformation.

Stage 2: Computation of local (per-particle) stress

In order to quantitatively predict the spatial distribution of the local mechanical properties in the PNC, the stress and strain fields (herein referred to as the local stress and strain) need to be computed at the atomic level resolution (see the flowchart of Fig. 1).

In accordance with Harasima’s definition of the local stress tensor, in which the stress due to the interaction of two particles is equally distributed between the regions where the particles reside [17], the distribution of stress within the PNC can be straightforwardly computed by the atomic Virial formalism, namely:

\[
\sigma_{i\alpha\beta} = -\frac{1}{V_i} \left[ m v_i \nu_{i\beta} + \sum_{\text{pairs}} \left( r_{i\alpha} F_{\text{pair}, \beta} + r_{j\alpha} F_{\text{pair}, \beta} \right) + \frac{1}{2} \sum_{\text{bonds}} \left( r_{i\alpha} F_{\text{bond}, \beta} + r_{j\alpha} F_{\text{bond}, \beta} \right) \\
+ \frac{1}{2} \sum_{\text{angles}} \left( r_{i\alpha} F_{\text{angle}, \beta} + r_{j\alpha} F_{\text{angle}, \beta} + r_{k\alpha} F_{\text{angle}, \beta} \right) \\
+ \frac{1}{4} \sum_{\text{dihedrals}} \left( r_{i\alpha} F_{\text{dihedral}, \beta} + r_{j\alpha} F_{\text{dihedral}, \beta} + r_{k\alpha} F_{\text{dihedral}, \beta} + r_{l\alpha} F_{\text{dihedral}, \beta} \right) \\
+ K_{\text{space}} r_{i\alpha} F_{\beta} + \sum_{n=1}^{N_i} \left( r_{i\alpha} F_{\beta} \right) \right].
\]  

where the indices \( i, j, k \) and \( l \) denote atoms, and \( \alpha \) and \( \beta \) the indices corresponding to the 3D Cartesian coordinate system \((x, y, z)\). Eq. (1) contains contributions from the kinetic energy (proportional to the mass and the velocity \( v \)) and contributions from pairwise non-bonded interactions (proportional to the position \( r \) and the interaction force \( F \)), bond stretching, bond angle bending, and dihedral torsional potentials, a K-space contribution from long-range Coulombic interactions and finally there is a term for the \( N_i \) fixes that apply internal constraint forces to atom \( i \). \( V_i \) is the atomic volume of atom \( i \). The latter is rather ill-defined, therefore typically the per-atom Virial contribution \( \sigma_1 V_i \) is calculated, and then averaged over the specific domain of interest.
We should also note that the proposed method can be also applied if the Hardy [17] or the Irving and Kirkwood [22] formalisms are used to compute local stresses. We expect that the results will not change, since we focus on the computation of mechanical properties relying on stress gradients. We shall notice that both of these alternative formalisms provide a definition of the local stress tensor by starting from a statistical mechanical derivation of the equations of hydrodynamics and by assuming a special localization for the particles that contribute to the inter-particle force.

Stage 3: Computation of local (per-particle) strain

A key component of NANOMEC involves probing directly the spatial distribution of the strain field at the atomic level for the systems under study. Such a distribution can be used in order to both predict directly the local mechanical properties and to parametrize accurate multi-phase continuum models.

The strain distribution is computed by using concepts from continuum mechanics to define the strain per atom, relating the kinematics and the positions of atoms at an initial time \( t_0 \) and at a subsequent time \( t_1 \). The coordinate vectors of atoms in the initial reference configuration \( \Omega_0 \) at time \( t_0 \) having a Cartesian basis \( \mathbf{e}_i \), and in the configuration \( \Omega_1 \) at time \( t_1 \) with a Cartesian basis \( \mathbf{e}_i \) are represented by \( \mathbf{X} \) and \( \mathbf{x} \), respectively (Fig. 2). Then the mapping from position vector \( \mathbf{X} \) to \( \mathbf{x} \), is denoted by \( \Lambda \) so that

\[
X = X_i \mathbf{e}_i; \ x = x_i \mathbf{e}_i; \ x = \Lambda(X),
\]

for some coordinates \( X_i \) and \( x_i \) in their respective basis vectors. Assuming sufficient continuity, the local deformation at the spatial point \( \mathbf{X} \) is characterized as the gradient of the mapping function motion and defined as

\[
F \approx \frac{\partial \Lambda}{\partial \mathbf{X}} = \frac{\partial \mathbf{x}}{\partial \mathbf{X}}
\]  \hspace{1cm} (3)

The deformation of an infinitesimal segment \( \partial \mathbf{x} \) at a point in the initial configuration can be expanded as a Taylor series. When the higher-order terms are omitted, \( \partial \mathbf{x} \) can be written as

\[
\partial \mathbf{x} = \Lambda(X + \partial \mathbf{X}) - \Lambda(X)
\approx \nabla \Lambda(X) \partial \mathbf{X} = F \partial \mathbf{X}
\]

It is expected that the local strain rate, defined per atom, for a specific atom \( m \) is determined by the deformation of its local environment, i.e. the changes in the relative position of all its neighboring

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**Fig. 2.** Schematic showing snapshots of neighboring atoms at times \( t_0 \) and \( t_1 \), with position vectors \( \mathbf{X} \) and \( \mathbf{x} \) in reference configurations \( \Omega_0 \) and \( \Omega_1 \), respectively.
atoms. Let’s assume that an atom \( m \) is located at position \( \mathbf{X}^m \) in the reference configuration \( \Omega_0 \) and position \( \mathbf{x}^m \) in the current configuration \( \Omega_1 \). Then, the position of neighboring atom \( n \) relative to that of atom \( m \) in each configuration is related to the deformation gradient \( \mathbf{F}^m \) of atom \( m \) according to

\[
\Delta x^{mn} = x^n - x^m, \\
\Delta X^{mn} = X^n - X^m, \\
\Delta x^{mn} = \mathbf{F}^m \Delta X^{mn}.
\] (5a) (5b) (5c)

with the requirement that Eq. (5c) holds for all neighboring atoms \( n \) of some reference atom \( m \). In other words, for each atom, \( \mathbf{F}^m \) must be determined from all its neighboring atoms so that pairwise interactions are accounted for. Thus, unlike in the continuum limit, \( \mathbf{F}^m \) can only be defined in a least-squares sense, seeking an optimal local deformation gradient \( \mathbf{F}^m \) per atom, namely

\[
\mathbf{F}^m = \arg\min_{\mathbf{F}^m} W^m(\mathbf{x}, \mathbf{X}, \mathbf{F}^m).
\] (6)

i.e. \( \mathbf{F}^m \) minimizes the squared error, given by

\[
W^m(\mathbf{x}, \mathbf{X}, \mathbf{F}^m) = \sum_{n=1}^{N} (\Delta x^{mn} - \mathbf{F}^m \Delta X^{mn})^T (\Delta x^{mn} - \mathbf{F}^m \Delta X^{mn}),
\] (7)

where \( N \) is the number of neighboring atoms within a maximum cut-off distance, \( r_{\text{cut}} \), which here is taken to be about 0.5-1 nm. Since this is a linear regression problem with respect to the deformation gradient, \( \mathbf{F}^m \) may be obtained directly from the normal equation that gives the minimizer to the cost function in Eq. (7). Hence, the nine components of the tensor \( \mathbf{F}^m \) can be obtained from the following linear system of equations:

\[
\begin{pmatrix}
I_3 \otimes \Delta \mathbf{X}^{mn} \\
\end{pmatrix}
\begin{pmatrix}
\Delta \mathbf{X}^{mn} \\
\end{pmatrix}^T \text{Vec}(\mathbf{F}^m) = \text{Vec}
\begin{pmatrix}
\Delta \mathbf{X}^{mn} \\
\end{pmatrix}^T \begin{pmatrix}
\Delta \mathbf{X}^{mn} \\
\end{pmatrix}.
\] (8)

where \( \text{Vec} \) performs a row major vectorization of its argument and \( I_3 \) is the \( 3 \times 3 \) identity matrix. Note that, in the above formulation, \( \Delta \mathbf{X}^{mn} \) and \( \Delta \mathbf{x}^{mn} \) are cast as \( 3 \times N \) matrices. When \( W^m \) is minimized, the parameters \( F_{ij}^m \) are the components of the optimal deformation gradient tensor. After \( F_{ij}^m \) is determined by solving Eq. (8), the Green-Lagrange strain tensor \( \mathbf{E}^m \) is defined with respect to the reference coordinates at time \( t_0 \) and in terms of \( \mathbf{F}^m \) as

\[
\mathbf{E}^m = \frac{1}{2} \left( \mathbf{F}^m (\mathbf{F}^m)^T - \mathbf{I} \right).
\] (9)

noting that for each atom \( m \) within the simulation box, \( \mathbf{E}^m \) is a symmetric \( 3 \times 3 \) symmetric tensor.

Stage 4: Averaging over specific domains of interest

From the solution to the least squares problem, the averaged kinematic quantities \( \mathbf{E}^m \) (calculated from Eq. 9) can be obtained for every atom in the system. Hence, for each deformation step, we compute the local strain for each subdomain \( \Omega \) from the average strain of all atoms within \( \Omega \), and obtain the average local stress within \( \Omega \) using

\[
\sigma_{\Omega_{\alpha\beta}} = \frac{1}{V^\Omega} \sum_{n=1}^{N_{\text{atoms}}} V_n \sigma_{\alpha\beta}^n,
\] (10)

where \( N_{\text{atoms}} \) is the total number of atoms in the subdomain of analysis \( \Omega \), and \( V^\Omega \) its volume.

Stage 5: Computation of mechanical properties within heterogeneous nanostructured systems

The above steps lead to the computation of the stress and strain distribution, within a specific domain, for a given deformation. To compute the mechanical properties, typically the stress vs strain data are needed. Therefore, steps 2, 3 and 4 are repeated for various applied deformations.
The mechanical properties for a subdomain of analysis can be obtained through the stress-strain curves. Moreover, using the strain tensor calculated in Eq. (9), the lateral deformation in the y direction as a function of the local tensile strain in the x direction can be plotted. The same procedure can be followed for other types of deformation, i.e., for tensile and/or shear loads. For example, the Young's Modulus $E_{xx}$ can be obtained from the slope of the stress-strain data in the linear elastic regime, by applying deformations in the x direction, whereas the Poisson’s ratio $v_{xy}$ can be determined from the slope of lateral deformation in the y direction as a function of the tensile strain in the x direction.

**Application**

NANOMEC can be used in any multi-component nanostructured system. To highlight the use of the proposed methodology, we apply the computational methodology for atomistic model PNCs. Our goal is to examine spatial distributions of the mechanical properties of heterogeneous PNCs defined at the local (atomic) level. As an example, here we consider a glassy polybutadiene/silica (PB/Silica) PNC system, consisting of 4.25 wt% silica (SiO$_2$) NPs, (corresponding to a volume fraction of $V_{NP} = 1.7\text{vol}\%$). The polymer matrix consists of 276 cis-1,4 PB chains of 100 monomers length (molecular weight of polymer matrix is 5400 g/mol), whereas the (cubic) simulation box has a size of $L = 125$ Å; see Fig. 2(a) for a typical snapshot of the model PNCs. More details about the atomistic model and simulations can be found elsewhere [21,23].

**Initialization: preparing the sample PNC**

In order to prepare sample PNCs, we consider several (five in this case) independent uncorrelated and well-equilibrated atomistic configurations, which are obtained via long atomistic MD simulations corresponding to a few $\mu$s at a high temperature ($T = 413K$) [21,23]. In order to improve statistics, larger model systems are then created by replicating the simulation box twice in each direction, and equilibrating the whole system via additional short MD runs. Finally, the system is cooled to 150 K with a cooling rate of 10 Kns$^{-1}$, which is well below the glass transition temperature (about 200K for cis-1,4-PB). In all MD simulations, PBCs are applied in all directions with a time step of 1 fs for integrating the equations of motion, truncating non-bonded interactions after a cutoff radius $r_{cut}=1\text{nm}$ and applying dispersion tail corrections for the energy and pressure.

**Stages 1 to 3: Computation of stress and strain fields**

After preparing the glassy PNC samples, stage 1 (see Fig. 3a) follows by applying uniaxial deformation with a constant strain rate of $\dot{\varepsilon}_{xx} = 3 \times 10^{-6}$ fs$^{-1}$. For this system, the subdomains considered are the NP region of radius 18.5 Å, the interphase region surrounding the NP extending to a radius 26 Å, and the polymer matrix that makes up the rest of the simulation box. The effect of the strain rate is not expected to be important, because we consider temperatures for which $T << T_g$. A snapshot of the deformed PNC under applied strain is shown in Fig. 3b. After each incremental step, the stress and strain per atom within the PNC structure are computed in accordance with stages 2 and 3 in the computational methodology (Fig. 1).

**Stage 4: Averaging and visualizing local strain fields over specific regions of interest**

The distribution of local strain fields under deformation can be visualized using slices through the domain. Each slice is then decomposed into cubic boxes of length 6 Å, and averaging is performed within each box. The output of this calculation is shown in Fig. 4a, where we show the distribution of the local strain under an applied global strain of $\dot{\varepsilon}_{xx} = 0.06$ (in the linear regime) for a slice passing through the center of a single NP, which is chosen randomly among the NPs present in the PNC system. Fig. 4a shows that the strain distribution in PNCs is non-affine, observing appreciable deviations from the applied strain. NP hardly deforms due to its high rigidity, whereas the strain within the polymer matrix is approximately equal to the globally applied one. However, the local
strain within the polymer/NP interfacial region varies significantly, attaining higher values compared to the matrix region. In contrast, the strain within homogeneous bulk systems broadly follows the affine deformation assumption, i.e. the values of the local strain are narrowly distributed around the applied global strain (Fig. 4b). To improve the statistical accuracy of the computation of local strain, this analysis may be repeated over several uncorrelated atomistic PNC configurations. Moreover, in order to study the effect of $r_{\text{cut}}$ on the local strain, we present in Fig. 5 the local strain as a function of $r_{\text{cut}}$ for different regions mentioned before. We can conclude, from Fig. 5a that the local strain converges after distance of $r_{\text{cut}}=8\,\text{Å}$, which also corresponds to the first minimum in the non-bonded (excluding bond, angle and dihedral correlations) radial distribution function in Fig. 5b. Therefore, we choose this value when computing the strain defined per atom level.

Stage 5: Computing the distribution of mechanical properties

In this stage, the distribution of the mechanical properties within the PNC system is calculated by computing the average stress strain fields in a specific subdomain (Interphase, matrix). In accordance with stage 4, the average local stress within each subdomain (here polymer/NP interphase and matrix) is calculated, by averaging the strain following each increment, as shown in Fig. 6.
Fig. 5. a) Strain data for Interphases and the bulk-like matrix region as a function of $r_{\text{cut}}$ distance. Data for the average of local strain is also shown, b) non-bonded pair radial distribution function of the PNC system.
Fig. 6. Stress–strain data for Interphases and the bulk-like matrix region. Data for the bulk (homogeneous) PB is also shown.

Fig. 7. Average local and global strain in function of steps. Each step corresponds to $\dot{\varepsilon}_{xx} = 3 \times 10^{-6} \text{ fs}^{-1}$.

The Young’s modulus for each region can be obtained from the slope of the stress–strain curve in the elastic regime (see Fig. 6). Due the low volume fraction of NPs (1.7%), the matrix region in the PNC behaves like in the case of the homogeneous bulk phase, as expected, noting that, the matrix region will become stiffer for higher volume fractions, owing to the changes in the conformation types. We also observe that, as alluded to earlier, the polymer/NP interphase is more rigid than the matrix due to the strong interaction between PB and the Si atoms.

Validation of the methodology

Finally, to validate the methodology for the computation of strain, we computed the averaged local and global strains, as well as the strain within the matrix region as functions of the applied (global) deformation steps, focusing on the elastic regime (see Fig. 7). The averaging for the local strain is performed for all atoms in the model, including the NP atoms. We observe that the average local strain is very close to the globally applied strain, which is compatible with the first law of thermodynamics with a relative error that does not exceed 6% after 8000 steps. Also noteworthy is
that the average strain in the matrix region is also very close to the global strain, which is consistent with the affine deformation assumption within the bulk material.

**Software detail**

NANOMEC is implemented in Python. Two scripts have been prepared to illustrate the workflow involved in the methodology presented in this study. The first one takes as input a trajectory derived from an MD simulator (here the LAMMPS output format is assumed) and calculates the local strain for all the atoms of a user specified configuration. The relative positions $\Delta X^m$ and $\Delta x^m$ of Eq. 5 are first calculated. Afterwards, $W^m$ of Eq. 7 is minimized to yield $F^m$ as shown in Eq. 8. The 9 components of the tensor $F^m$ can be obtained from the linear system in Eq. 8. Finally, $E^m$ is calculated from $F^m$ as in Eq. 9. Using the linear system method, the computation time for obtaining the strain distribution within a frame is approximately 3 sec /1000 atoms, using one core of an i7-3540M cpu @ 3.00GHz.

The lengthy calculations are performed in parallel using the MPI library through mpi4py. The coordinates of each configuration are scattered along cpus and each cpu is assigned a range of m's (a set of atoms) to calculate. When the partial calculations are complete the strains are gathered back from the different cpus. This parallelization method is straightforward, following a massively parallel paradigm, while almost no communication is needed among cpus. Thus large numbers of cpus can be utilized to reduce the computation time without incurring significant overhead. Note that Numba is also used to further accelerate the code.

The calculated strain per atom is saved in a NumPy binary file to make it available to other user scripts for analysis. We do not provide a generic analysis tool of the results. Instead we provide a second script as an example of how one might want to inspect and visualize the results of the calculation script. The second script takes as input the output of the first script, the local strain per atom, and spatially aggregates the results into cubic boxes of user defined edge length. The results are then visualized through a heatmap plot. A small sample trajectory of a Silica nanoparticle embedded in Polybutadiene matrix is provided with the code, so that one can immediately perform a trial run and inspect the results. A Jupyter Notebook is provided to illustrate the procedure that is used to calculate the atomistic strain from a LAMMPS trajectory, which also includes a set of commands for visualization.

**Conclusion**

NANOMEC refers to a computational methodology that directly computes the distribution of the local stress and strain of atomistic model PNCs under a globally applied external strain field. The local, atom-based stresses are obtained by invoking the standard Virial formalism based on Harasima’s formulations. Drawing inspiration from continuum mechanics, the proposed approach allows us to compute the distribution of strain fields within a PNC, by computing an atomic-level deformation gradient, which accounts for the influence of the immediate neighborhood on some reference atom. Within this framework, local stress-strain data can be obtained separately for the interphase and the matrix region, whereas the computed strain distribution may be visualized using 2D slices through the PNC domain.

A set of python scripts used to calculate and visualize the atomistic strain of a molecular trajectory can be founded: [https://github.com/SimEA-ERA/NANOMEC.git](https://github.com/SimEA-ERA/NANOMEC.git).

A general description about the strain calculation tools is presented followed by an example of molecular system. A detail about the usage of the python code including several command line options control the calculation and the visualization is presented.

**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Data availability**

We have shared the link to our data at the attached file.
Acknowledgements

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 101030430. The work was supported by computational time granted from the Greek Research & Technology Network (GRNET) in the National HPC facility ARIS under a project named NANOMEC. The work was also supported by Cyl High Performance Computing Facility (HPCF) under a project named NANOMEC. We acknowledge support by project “SimEA”, funded by the European Union’s Horizon 2020 research and innovation programme under Grant Agreement No. 810660.

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