

A coupled MD-FE methodology to characterize mechanical interphases in polymeric nanocomposites

Maximilian Ries^{a,b,*}, Gunnar Possart^{a,c}, Paul Steinmann^{a,d}, Sebastian Pfaller^{a,e}

^a*Institute of Applied Mechanics, Friedrich-Alexander-Universität Erlangen-Nürnberg*

^b*maximilian.ries@fau.de*

^c*gunnar.possart@fau.de*

^d*paul.steinmann@fau.de*

^e*sebastian.pfaller@fau.de*

Abstract

The mechanical properties of polymeric nanocomposites often cannot be determined from the involved components' properties by just using classical mixing rules. To address this problem, the concept of *interphases* provides an elegant explanation since it accounts for and builds on the comparatively large surface-to-volume ratio of the nanoparticles. Interphases denote those regions in the polymer matrix whose mechanical properties are influenced by the filler surfaces and therefore deviate from the bulk polymer properties. The determination of the corresponding property gradients inside the interphases poses considerable, often hardly solvable, challenges to the experimenter and is thus still an unsolved problem in many cases. We, therefore, present a method to identify elastic and inelastic property gradients in polymeric interphases around nanoparticles. In the sense of a quasi pseudo-experimental approach, a horizontally coupled MD-FE simulation method for amorphous polymers developed by us is used to determine the deformation behavior of volume elements consisting of a polymer matrix and two nanoparticles with varying initial distances. Using an appropriate strain measure and an FE-based inverse parameter identification, the spatially dependent material parameters in the polymeric interphase around the nanoparticles are determined. It turns out that not only the elastic

*Corresponding author

properties of the matrix polymer form gradients. Above all, also the inelastic characteristics such as the yield stress are affected. These results are of significant importance for the engineering of both nanocomposites and corresponding adhesive formulations.

Keywords: polymer nanocomposites; interphase layers; interphase properties; atomistic-continuum coupling

Highlights:

- Numerical study of mechanical interphases in polymer nanocomposites
- Uniaxial deformation via atomistic-continuum coupling method
- Identification of material property gradients inside the interphase
- Revealing elastoplastic behavior in the vicinity of filler particles

1. Introduction and outline

The concept of *interphases* has been introduced based on experimental observations of the mechanical properties of adhesively bonded joints. These frequently show a strong dependence of the mechanical properties on the thickness
5 of the adhesive layer. Thereby, *interphase* denotes those regions of the polymer in the substrate's vicinity, in which the mechanical properties deviate from those of the undisturbed bulk material, i.e., far away from the substrate. These property changes are caused by the interactions of the substrate surface with the polymer network and are typically highly dependent on the material pairing
10 (epoxy on aluminum, polyurethane on steel, ...) [1, 2, 3, 4], the manufacturing conditions (curing temperature, humidity, ...) [5, 6, 7], and finally the application environment (temperature cycles, aging, ...) [8, 9, 10]. In the case of composites, where filler particles are embedded into the polymer matrix, one can assume that similar mechanisms lead to interphase-like shells surrounding
15 each filler particle [11]. Regarding the particular case of nanocomposites, the concept of interphases may well explain the frequent observation that their overall mechanical properties cannot simply be deduced from the properties of the constituents (particles and matrix) by classical mixing rules. Unlike microcomposites, for which these mixing rules have worked well, nanocomposites exhibit
20 a considerably larger surface-to-volume ratio, i.e. the impact of the volume content of the interphases surrounding the particles becomes dominant [12]. Hence, it is essential to have a detailed knowledge of the mechanical property gradients inside the interphases to allow for physically reasonable structure simulations of nanocomposites. A sketch of the interphase situation in nanocomposites is given
25 in Figure 1: Interphases can be described as spherical shells of finite thickness which surround the particles and show properties between those of the bulk and the particle materials.

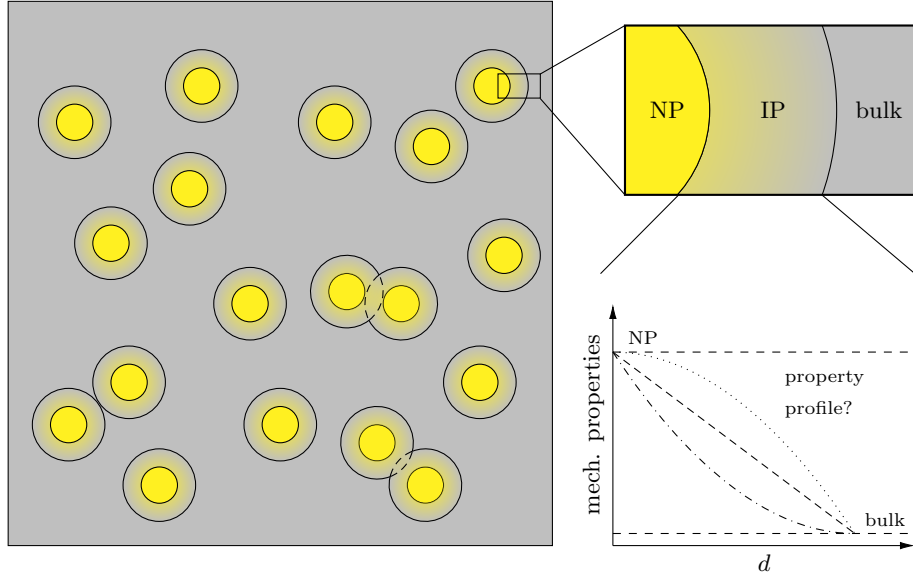


Figure 1: Schematic representation of interphases (IP) as forming between bulk polymer and nanoparticles (NP) and the corresponding mechanical property profiles.

Three questions immediately arise in this regard: (i) How thick are interphases, (ii) which mechanical properties are affected at all, and (iii) according to
 30 which functional relation are the properties changing from the particle surface towards the bulk polymer? Due to their particular location – one occasionally also speaks of *buried layers* – interphases usually pose a serious challenge to the experimenter, especially in the case of nanocomposites [13].

The outstanding properties and versatility of nanocomposites motivated
 35 many researchers to approach these questions from different directions. Experimental studies using small-angle X-ray (SAXS) scattering [14, 15], transmission electron microscopy [16, 17] were carried out to investigate the morphology of the interphases. Maghami et al. propose an experimental methodology to derive the interphase’s morphology, thickness, and permeability employing SAXS
 40 on polyethersulfone-silica composites [18]. Broadband dielectric spectroscopy (BDS) helps to reveal the dynamic behavior of polymers and is used to identify the glass transition temperature of the neat polymer and polymer nanocom-

posites [19]. Another handy experimental method is Brillouin light scattering (BLS), which has been commonly used to examine interphases [20, 21, 22] and, in the case of nanocomposites, allows the measurement of mechanical quantities such as Poisson’s ratio and Young’s modulus in the submicron range [23, 24, 25]. Holt et al. [26] used BLS to determine the bulk and shear moduli of P2VP-silica composites and compared the results for grafted and physically absorbed filler particles at comparable molecular weights. The non-grafted composite exhibits a more pronounced strengthening of the mechanical properties than the grafted one relative to the neat polymer. The authors attribute this strengthening to chain packing and stretching within the interfacial layer. Bulge tests of thin (≈ 100 nm) polymeric films [27] allow for the measurement of stress-strain behavior of polymer nanocomposites and thus identification of Young’s modulus, Poisson’s ratio, and yield strength [28, 29]. However, there are no direct methods to locally measure the properties of the interphase.

In order to predict the effective properties of polymeric composites, many empirical models, i.a. by Leidner et al. [30], and Pukanszky [31], have been developed for micron-sized additives taking into account the influence of filler size, filler content, matrix-filler interactions, and interfacial area. These models were thoroughly extended to address the challenges of nano-sized filler particles and performed well compared to experimental results [32, 33, 34, 35, 36]. In contrast to classical composites, the interphase is a crucial factor in nanocomposites [37, 38] and hence requires appropriate modeling, as in the three-phase model proposed by Ji et al. [39]. Using this model, Zare et al. [40, 41] subdivide the interphase into layers and conclude that a power law is best suited to predict Young’s modulus spatial profile for various polymeric nanocomposites.

Due to van der Waals interactions, the nanoparticles tend to form clusters, which increases the effective filler size. As a result, this agglomeration has a considerable influence on the fillers’ effectiveness and thus on the material properties of the composite. Consequently, considerable effort is devoted to the adequate modeling of this effect [42, 43, 44].

The outstanding properties of nanocomposites originate from complex mecha-

nisms at the molecular scale. Since the aforementioned empirical models can
75 only partially capture these, ab initio studies with molecular dynamics (MD)
have been conducted to unravel the interfacial region. Shandiz et al. [45] eval-
uate the density distribution within the interphase to generate homogeneous
samples at various density levels. Subjecting these samples to uniaxial tension
and identifying the respective Young’s modulus enables them to approximate the
80 interphase’s stiffness profile. Odegard et al. [46, 47] introduced the equivalent-
continuum modeling: A continuum mechanical constitutive law is calibrated by
matching its energy under deformation to the energy obtained in preceding MD
simulations under identical boundary conditions.

Due to MD’s spatial and temporal limitations, concurrent multiscale approaches
85 have been increasingly developed, aiming to combine the accuracy of fine-scale
methods with the efficiency of macroscopic descriptions. These approaches can
be categorized into hierarchical and partitioned-domain methods [48]. In hier-
archical methods, the coarse-scale provides the fine-scale boundary conditions
and, conversely, the fine-scale provides the constitutive law for the coarse-scale.
90 Here, both resolutions are applied simultaneously to the entire domain, result-
ing in the macroscopic material response as an average of the fine-scale, thus
also referred to as homogenization. A well-known example is the widely used
FE² method, where a fine-scale representative volume element (RVE) is eval-
uated at every quadrature point of the coarse-scale finite element (FE) model
95 [49, 50]. Recent advances in computational homogenization for nanocomposites
have been made, e.g., by Kumar et al., by comparing an interface-energetics-
enhanced approach with a graded-interphase-enhanced formulation to capture
the size-effect [51].

Partitioned-domain multiscale approaches have been introduced for crystalline
100 materials most prominently with the Quasicontinuum method [52, 53], the Ar-
lequin method [54, 55] or the Bridging Domain method [56, 57]. A thorough
overview of these atomistic-to-continuum coupling strategies can be found in
[48]. Based on the preceding methods, Pfaller et al. introduced the CAPRICCIO
method [58, 59, 60, 61, 62, 63, 64] for the treatment of amorphous polymers,

105 which we discuss in more detail in Section 2.1. A comprehensive overview of multiscale studies of polymer nanocomposites is given in [65, 66, 67].

In this contribution we propose a rather unconventional route to determine the spatially varying mechanical properties within the interphase: Contrary to the frequently used empirical models, we rely on an MD-based model of the polymer composites. To this end we apply the aforementioned CAPRICCIO
110 method (cf. Section 2.1) to perform physically sound deformation simulations of a polystyrene matrix containing silica nanoparticles. In particular, we consider systems with two particles located at several different initial distances, which turns out to provide a local strain measure well-suited to characterize polymeric interphases. In other words, we use multiscale simulations of specifically designed nanocomposite systems to substitute real experiments. Due to the underlying MD at the polymer-particle contact, these pseudo-experimental data can be assumed to naturally capture both the formation and the effects of the interphases. Based on these data, a FE (FE) based inverse parameter identification
120 procedure is applied afterward to identify and quantitatively determine the gradients of the inelastic mechanical properties around the nanoparticles. Figure 2 sketches the following content of this contribution.

The idea to utilize concurrent multiscale simulations of two-particle systems as described above has already been introduced in an earlier contribution of some
125 of the authors [68]. However, by that time, the setup and equilibration of the nanocomposites' initial MD description suffered from some minor unphysical constraints, which have meanwhile been resolved. Our previous observations are mainly reproduced by the new data presented in the following, except for systems with very close nanoparticles.

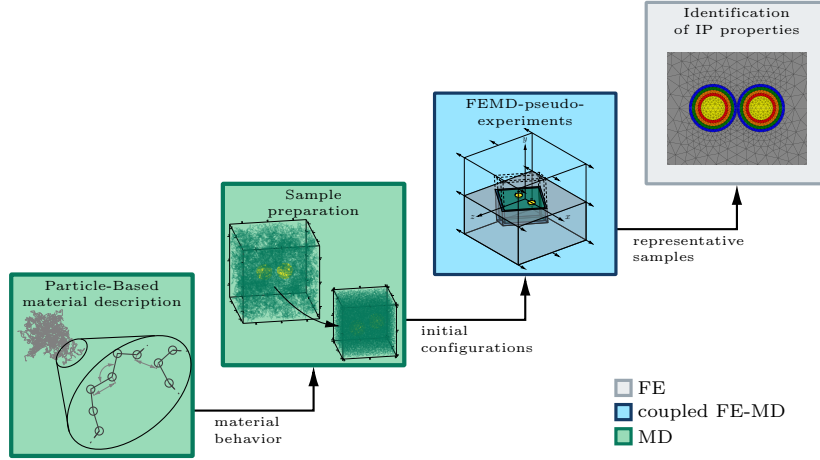


Figure 2: Graphical outline: The behavior of the investigated polymer is prescribed via a particle-based material description, which enables the preparation of our samples. The resulting initial configurations are used in subsequent, coupled MD-FE pseudo-experiments. Representative samples are chosen to identify interphase properties in an FE framework.

2. Coupled MD-FE pseudo-experiments

2.1. The Capriccio method

The Capriccio method is a recent multiscale technique, which is particularly designed for amorphous polymers. It has been developed in close collaboration between chemists and engineers [59, 60] and has recently been thoroughly optimized to reduce artifacts arising from the coupling of very different material modeling approaches [62]. The Capriccio method is, according to [48], a partitioned-domain technique that concurrently couples a discrete domain treated by MD and a continuum domain resolved with the Finite-Element-Method. A crucial aspect of the Capriccio method is introducing so-called anchor points, which are auxiliary particles responsible for the information transfer between the domains, cf. Figure 3 (left).

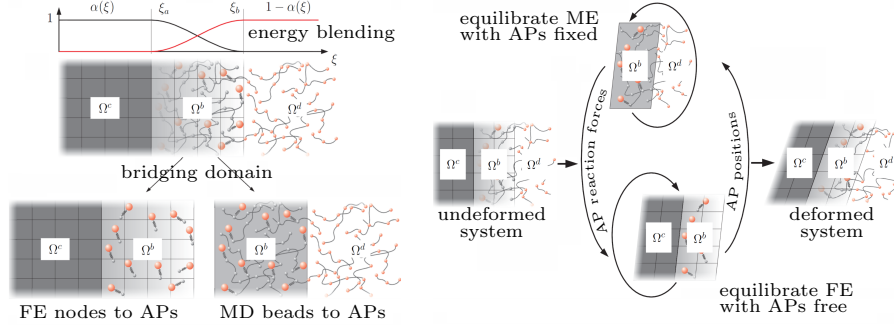


Figure 3: Capriccio method overview: Coupling of MD and FE domains through anchor points and elastic springs (left), information transfer between domains and staggered solution scheme (right).

From the MD point of view, these anchor points are spatially fixed and confine the MD particles to their designated domain. To this end, harmonic potentials are employed to define an interaction between anchor points and MD particles. By doing so, classical periodic boundary conditions (PBC) can be substituted by so-called stochastic boundary conditions (SBC). This concept has been described in detail in [58] and enables deforming the particle domain via the anchor points. To this end, the anchor points are coupled to the continuum in a weak sense and may change their spatial positions according to the continuum deformation. This anchor point to continuum coupling bases on the Arlequin method, introduced in the late 1990s by Ben Dhia [69], and realizes the coupling by blending the energies of the different domains in a bridging domain. A kinematic coupling constraint relates the continuum displacement field and the particle displacements in a weak sense. The Arlequin method, which was initially intended to couple FE domains of different resolutions, has later been extended to the coupling of continua with discrete, crystalline domains [54, 70].

The staggered algorithm used to solve the coupled problem is sketched in Figure 3 (right): Upon applying the first load step in the FE domain, the anchor points change their position according to the deformation of the continuum. Thus, they disturb the equilibrium in the particle domain, which has to be

re-equilibrated subsequently. This, however, renders updated forces the MD particles exert on the auxiliary anchor points, such that the following FE step requires adjusting the anchor point positions. After a certain number of MD-FE iteration steps, the system achieves equilibrium, and another load step can be
165 applied.

An appropriate coupling of MD and continuum domains requires that the material behavior of both descriptions fits together. To this end, a thorough characterization of the particle domain’s mechanical properties is required to enable choice and proper calibration of the constitutive law for the continuum.
170 Based on MD pseudo-experiments as detailed in [71, 72, 73], appropriate constitutive descriptions have been chosen, and an inverse parameter identification has been carried out [74]. A crucial aspect of this procedure is to carefully choose the load range in which the continuum model is valid: In general, larger deformations require more sophisticated models but enable to reduce the size of
175 regions to be treated entirely on the particle scale. Accordingly, the numerical effort can be reduced.

2.2. Sample preparation and simulation setup

In this contribution, an atactic polystyrene matrix with two embedded nano-sized silica particles is subjected to uniaxial tension. To this end, well-established
180 and computationally efficient coarse-grained force fields for both the polymer and the nanoparticles are used, which were derived via an Iterative Boltzmann-Inversion [75, 76]. Initially, the two nanoparticles, each consisting of 873 beads resulting in a diameter of $D_{\text{NP}} = 4 \text{ nm}$, are placed at different initial distances $\mathcal{L}_{\text{NP}}$ of 6 to 12 nm relative to each other. The surrounding 300 polystyrene
185 molecules are generated with 200 beads each using a self-avoiding random-walk algorithm [75]. Subsequently, a preparation procedure described in more detail in [71] is applied, where the samples are first equilibrated at high temperature and then cooled down below glass transition temperature using the MD software, IBIsCO [77]. Since the silica particles are not constrained during this
190 process, the resulting samples exhibit rather arbitrary locations and distances

of the nanoparticles inside the matrix polymer.

In contrast to the above steps, which are simulated under periodic boundary conditions, the coupled MD-FE scheme requires so-called stochastic boundary conditions [60, 58]. Therefore, polymer chains protruding beyond the simulation
 195 box are cut and relocated inside. Additionally, anchor points are inserted in the bridging domain to confine the MD particles to the simulation box and enable the data transfer between FE and MD computations [61, 62].

The samples are then embedded in a continuum cuboid of edge length $\mathcal{L}_{\text{FE}} = 50 \text{ nm}$, referred to as the FE domain. To compensate for the nanoparticles' arbitrary orientation, we rotate the MD system such that the connection vector
 200 of the two nanoparticles aligns with the global x -axis. Furthermore, a translation ensures that the center between the two particles coincides with the global coordinate origin resulting in a setup as shown in Figure 4.

To counteract the imbalance caused by the transition to stochastic boundary
 205 conditions, the samples are equilibrated once more, but now in the coupled MD-FE configuration and without any external loads.

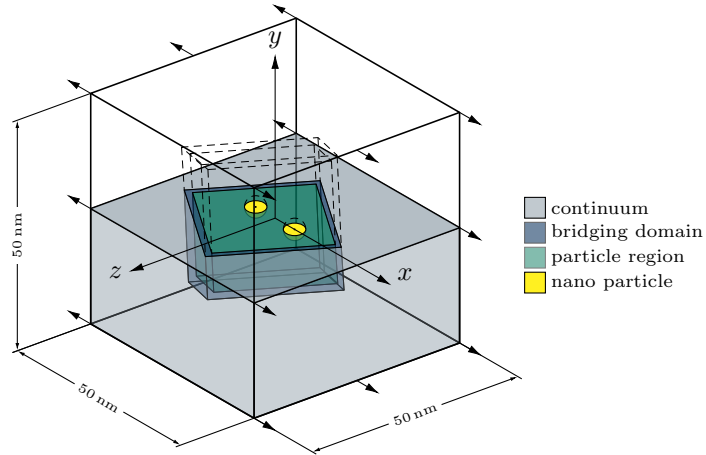


Figure 4: MD-FE simulation setup: A particle region comprising two nanoparticles and a polystyrene matrix, as well as its surrounding bridging domain are integrated into a continuum cuboid in such a way that the nanoparticles are aligned on the x -axis and their center coincides with the coordinate origin.

220 However, interparticle strain $\varepsilon_{xx}^{\text{NP}}$ reveals a clear dependence on initial particle distance $\mathcal{L}_{\text{NP}}$: Samples with initially close particles, i.e., with $\mathcal{L}_{\text{NP}}$ -values between 5 to 6 nm, provide (blue) curves that are clustered around small values and show only a slight linear increase with the applied overall deformation. This means that the particles stick together and do not follow the surrounding
 225 polymer's deformation, like if they are connected by a material much stiffer than the bulk – or by stiff interphases. Contrary to this, systems with more distant particles show larger initial values for $\varepsilon_{xx}^{\text{NP}}$, and the (yellow to red) curves increase significantly and nonlinearly with the applied overall deformation. In these cases, the soft bulk-like polymer is also located between the particles and
 230 increasingly deforms like the outer material. Consequently, interparticle strain $\varepsilon_{xx}^{\text{NP}}$ is well suited to detect and quantify differences in the deformation behavior that originates from the initial particle distance. It further indicates the ratio of bulk and interphase material located between the particles. This sensitivity predestines this measure for the characterization of interphases.

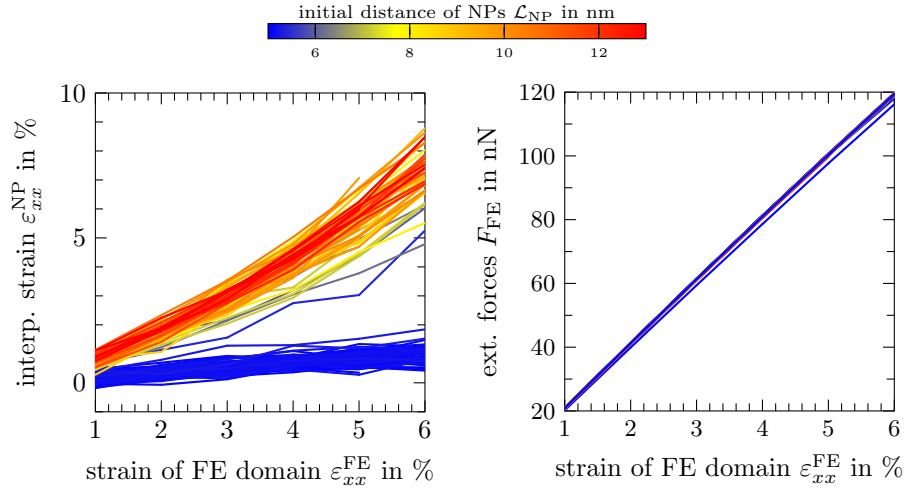


Figure 6: Influence of initial distance of NPs on uniaxial pseudo-experiments: Resulting external forces in deformation direction F_{FE} (right) and interparticle strain $\varepsilon_{xx}^{\text{NP}}$ (left), versus strain of FE domain $\varepsilon_{xx}^{\text{FE}}$, respectively.

235 3. Continuum-based identification of interphase property profiles

To exploit the above-presented results of the Capriccio pseudo-experiments for the characterization of interphases, purely continuum mechanical, FE discretized surrogate models of the two-particle nanocomposite specimens have been developed. By applying a typical parameter optimization scheme, these
 240 FE models then enable a quantitative determination of mechanical property profiles inside the interphases around the particles, based on the $\varepsilon_{xx}^{\text{NP}}(\varepsilon_{xx}^{\text{FE}})$ -data given in Figure 6 (left). The FE deformation simulations are thereby repeated with iterative adjustment of the material parameters inside the interphases until the interparticle strain profiles for two selected, representative configurations
 245 with initially close and distant nanoparticles are reproduced sufficiently well.

3.1. FE models and parameter optimization procedure

The FE models are fully three-dimensional, but symmetry is exploited in all three directions via appropriate boundary conditions to reduce computational costs. Figure 7 depicts a close-up of the nanoparticle(s) (yellow, 4 nm diameter)
 250 embedded in the polymer matrix (grey). Since Ghanbari et al. [78] have shown that the interphase for our systems comprises four monomer layers, we chose to represent this region through four separate, equally thick layers of finite elements, whereby each layer has its own set of material parameters. These interphase layers are denoted from IP1 (blue) next to the bulk polymer to IP4
 255 (red) at the particle surface. The thickness of each of these layers is chosen as 0.5 nm, adding up to an overall interphase thickness of 2 nm, which is in line with results from Ndoro et al. [79], Riccardi et al. [80], and Liu et al. [81], who reported disturbed structural properties of the polymer for only the first two nanometers away from the nanoparticle surface. Finer discretizations of
 260 the interphase with more layers, i.e. more sampling points to approximate the actual property profiles, are of course possible but imply correspondingly higher optimization efforts and longer computation times. For our purposes, four values are initially sufficient to capture the transition between the properties of bulk material and polymer at the particle surface.

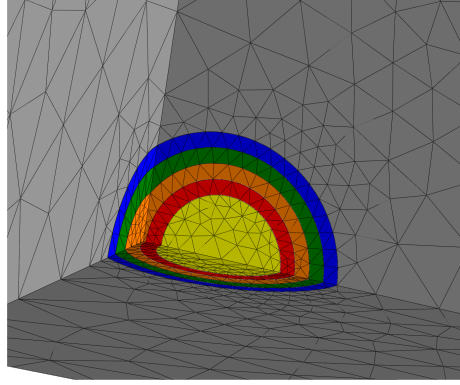


Figure 7: FE surrogate model of the Capriccio simulations: Close-up to the nanoparticle (yellow) and the surrounding four interphase layers IP1 at the bulk polymer (grey) to IP4 at the particle surface. Symmetry is exploited with respect to the three front planes via appropriate boundary conditions.

265 Bulk polymer, interphase layers, and particles are discretized with quadratic tetrahedral elements (Abaqus: C3D10) and such that conforming meshes result, i.e. there are no hanging nodes between the different domains, but the neighboring domains share all nodes at the interfaces. Consequently, all interfaces between bulk polymer, interphase layers, and nanoparticles are tied,
 270 i.e. no contact description is required, and there are no relative lateral displacements, friction, or separations, which correctly reproduces the situation of the Capriccio pseudo-experiments.

The selected finite element size or mesh density naturally is a compromise between computation time and accuracy. All FE models used here consist of
 275 approximately 10 000 elements with about 17 000 nodes, see Figure 7. It has been verified within the scope of a small convergency study that the relevant quantities F_{FE} and interparticle strain ε_{xx}^{NP} improve only in the low per mille range when even finer meshes are used.

The comparably stiff silica nanoparticles are treated by small strain linear elasticity with Young's modulus $E_{NP} = 162.1$ GPa and Poisson's ratio
 280 $\nu_{NP} = 0.272$, which is in line with corresponding values available in the relevant literature. For the bulk polymer, the simplest hyperelastic large strain

formulation, i.e. the NeoHookean material model [82], is initially used. This constitutive law is natively implemented in Abaqus and considered sufficient for the purposes relevant here, although there are, of course, much more sophisticated models available for polystyrene. The elasticity constants of the bulk polymer $E_0 = 842.756$ MPa and $\nu_0 = 0.3$ have been identified from MD simulations of uniaxial tension tests and translate to $c_{10} = 162.068$ MPa and $d_1 = 0.002848$, which are the corresponding material parameters required by Abaqus. The four interphase layers are treated by the same material model as the bulk polymer, but each have individual material parameters $E_{1...4}$ and $\nu_{1...4}$, which are subject to optimization with respect to the Capriccio $\varepsilon_{xx}^{\text{NP}}(\varepsilon_{xx}^{\text{FE}})$ -data.

In the following, two selected but representative cases for a system with initially very close and a system with initially more distant nanoparticles are chosen out of the available Capriccio data presented in Subsection 2.3, Figure 6 (left). In the *close case*, the particle centers have an undeformed distance of $\mathcal{L}_{\text{NP}} = 5.18$ nm, i.e. the two interphases are strongly overlapping, compare Figure 8 (left), which shows the corresponding surrogate FE model. In the *distant case*, initial particle distance $\mathcal{L}_{\text{NP}} = 7.95$ nm and the two interphases touch each other only slightly, see Figure 8 (right).

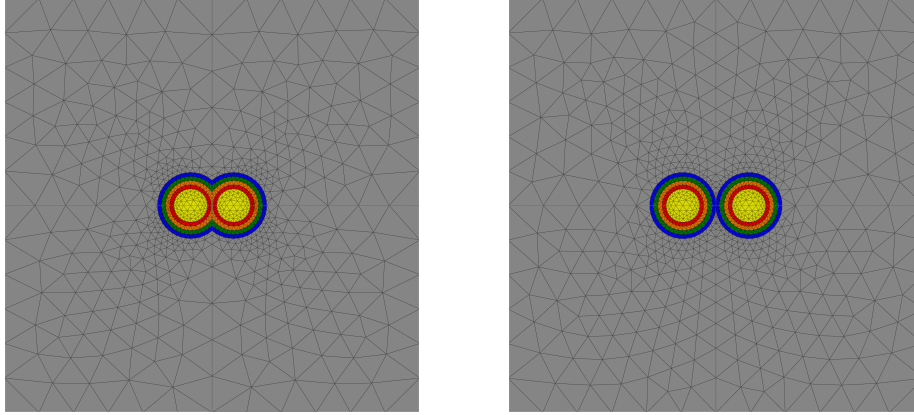


Figure 8: FE surrogate models for two representative cases of the Capriccio pseudo-experiments: 2D-cut of the *close* (left) and *distant* (right) case, cut through the center plane. Deformation and force are applied and measured in horizontal direction, respectively.

Both surrogate models cover an overall simulation domain of $[50 \text{ nm}]^3$ and precisely reproduce the deformation histories of the corresponding Capriccio simulations and provide the same output quantities, i.e. the overall reaction force F_{FE} in the horizontal direction and the deformed interparticle distance ℓ_{NP} ,
 305 which allows the computation of interparticle strain histories $\varepsilon_{xx}^{\text{NP}}(\varepsilon_{xx}^{\text{FE}})$ according to Equation (1). For the sake of simplicity, the latter are now normalized with respect to the applied overall strain $\varepsilon_{xx}^{\text{FE}} = [\ell_{\text{FE}} - \mathcal{L}_{\text{FE}}]\mathcal{L}_{\text{FE}}^{-1}$ with $\mathcal{L}_{\text{FE}} = 50 \text{ nm}$, i.e. *normalized interparticle strain* histories

$$\tilde{\varepsilon}^{\text{NP}} = \frac{\varepsilon_{xx}^{\text{NP}}}{\varepsilon_{xx}^{\text{FE}}} \in [0, 1] \quad (2)$$

are used to build the objective (or goal) function required by the optimizer
 310 to determine interphase property profiles. In the limiting case $\tilde{\varepsilon}^{\text{NP}} = 1$, the two particles exactly follow the deformation of the surrounding polymer, like it would be the case when there is enough undisturbed bulk polymer in between them to compensate for possibly much stiffer interphases. Vice versa, in the limiting case $\tilde{\varepsilon}^{\text{NP}} = 0$, the particles do not move at all with the surrounding
 315 polymer, as if they were glued together due to overlapping interphases with a much larger stiffness.

Figure 9 (left) depicts the resulting $\tilde{\varepsilon}^{\text{NP}}$ -profiles for the considered close and distant cases. While the former shows a roughly constant value of around 0.25, indicating particles that are mainly sticking together, the latter is more or less
 320 continuously growing from 0.6 to about 0.9, i.e. the, particles deform increasingly better with the surrounding polymer. To ensure the roughly linear elastic force response as measured by the Capriccio pseudo-experiments, the goal function additionally contains one of the two corresponding, almost identical force-strain curves as depicted in Figure 9 (right).

325 Both FE surrogate models (Figure 8) and the objective functions (Figure 9) are now used in an inverse parameter identification scheme to optimize the mechanical properties of the four interphase layers IP1...4. In an iteration loop, the two FE simulations are simultaneously carried out with Abaqus, the reaction forces and interparticle strains are subsequently extracted using a Python script

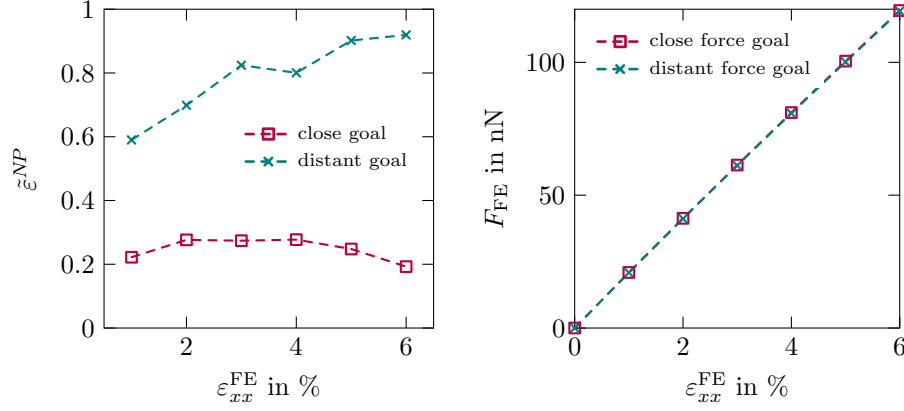


Figure 9: Components of the objective function used by the optimizer to determine mechanical property profiles inside the interphases: Normalized interparticle strain histories $\hat{\varepsilon}^{\text{NP}}$ (left) for the close and distant cases and corresponding overall reaction force curves (right).

330 and then transferred to an optimization routine available in Matlab. (*lsqcurvefit*, a gradient descent method optimizer with finite differences for the computation of the sensitivities) iteratively updates the interphase layers' material parameters until the deviation from the objective function falls below a prescribed threshold. The arithmetic mean

$$\Delta = \frac{1}{n} \sum_{i=1}^n \sqrt{[\hat{\varepsilon}_{i,\text{goal}}^{\text{NP}} - \hat{\varepsilon}_{i,\text{fit}}^{\text{NP}}]^2} \quad (3)$$

335 quantifies the deviation between the goal and the fit curves of the interparticle strain with number of data points n comprising the close and distant case. The results of four of these procedures with increasingly complex constitutive descriptions of the interphases are discussed in the following subsections.

3.2. Homogeneous elastic material without interphases

340 The first result considers a homogeneous, elastic polymer without any interphases, i.e. we do not perform a parameter optimization but only simulate the two cases using the bulk parameters constant in all four interphase layers:

$$E_{1\dots 4} = E_0 = 842.756 \text{ MPa} \quad , \quad \nu_{1\dots 4} = \nu_0 = 0.3 \quad (4)$$

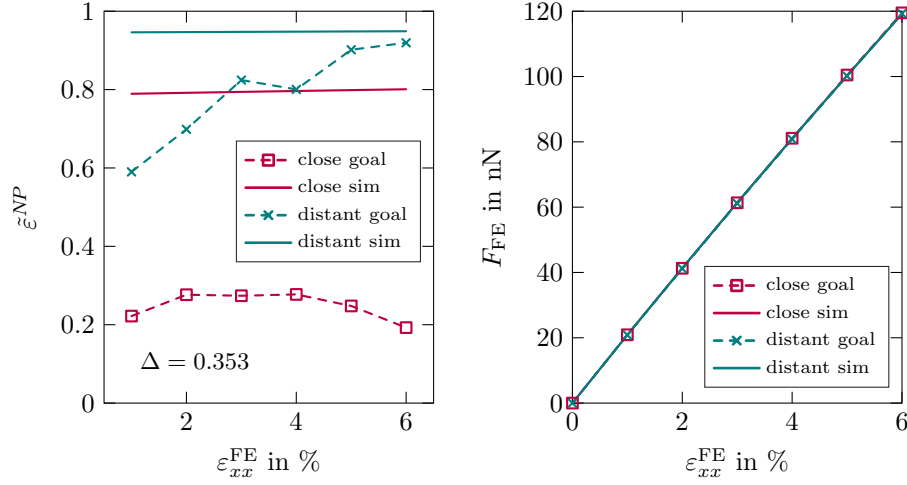


Figure 10: FE simulation results vs. Capriccio data for the close and distant cases, assuming homogeneous elastic material without interphases: Profiles of normalized interparticle strain (left) and overall force (right).

Figure 10 compares the resulting $\bar{\epsilon}^{NP}$ -profiles and force responses to the corresponding goal data. While the force curves are perfectly matching, see
 345 Figure 10 (right), the interparticle strain profiles are both missed by far, quantitatively as well as qualitatively ($\Delta = 0.353$). Both cases provide roughly straight lines, which are independent of the overall strain. One can obviously identify a purely geometrical effect of the different initial particle distances already for a homogeneous polymer matrix, which is reflected by the offset of about 15%
 350 in level between the two curves. Even without any interphases present, the initially closer particles tend to stick together more than their counterparts being farther away. The latter deform similarly to the outer matrix, i.e. $\bar{\epsilon}^{NP}$ is close to one, whereas the former reach only about 80% of this value. Despite this purely geometric effect, both $\bar{\epsilon}^{NP}$ -curves are still far away from their goals, not
 355 only in terms of magnitude but in the distant case also in terms of shape. This implies the necessity to increase the structural and constitutive complexity of the models.

3.3. Elastic material with linear property profiles inside the interphases

The polymer is still treated as hyperelastic, but we now allow different elasticity parameters inside the four interphase layers. It turns out that a simultaneous, free optimization of all eight interphase parameters works poorly and is highly dependent on the selected starting values. For the sake of simplicity, we thus assume that Young’s modulus and Poisson’s ratio can change linearly from the bulk values towards the particle surface, whereby both an increase or a decrease are allowed. The optimizer hence has to determine only the two slopes for E and ν , resulting in the following optima:

$$E_4 = 5.30197 \cdot E_0 = 4468.27 \text{ MPa} \quad , \quad \nu_4 = 1.6 \cdot \nu_0 = 0.48 . \quad (5)$$

The increase in ν has been artificially limited to a factor of 1.6 to avoid locking problems. An increase of Young’s modulus by a factor of 5.3 turns out to be the best option to capture both cases simultaneously as well as possible. A separate optimization for the close and distant cases would, of course, provide different values, which then fail even more in reproducing the complementary case. Figure 11 depicts the corresponding linear profiles of E and ν inside the four interphase layers, in each of which both values are piecewise constant. The increase in stiffness is an expected result in view of the pseudo-experimental Capriccio data, which indicated that the particles are sticking together stronger the smaller their initial distance. A growth of Poisson’s ratio towards the surface can also be considered reasonable since lateral contractions of the polymer are increasingly hindered in the vicinity of the stiff particles.

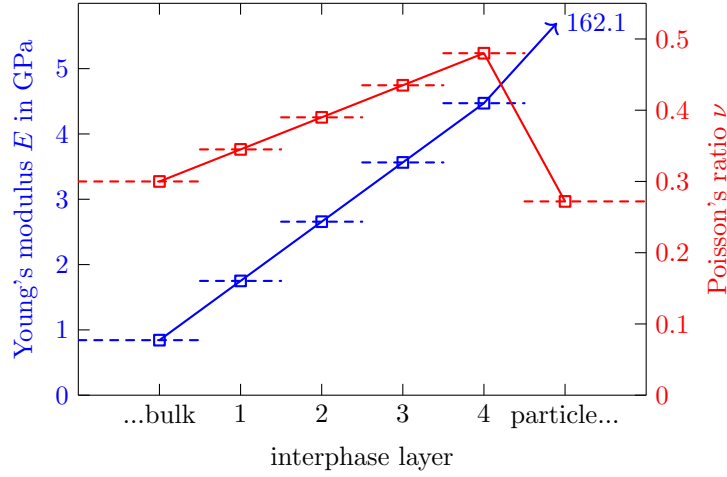


Figure 11: Optimal linear profiles for the elasticity parameters inside the interphases.

Figure 12 compares the resulting $\tilde{\varepsilon}^{\text{NP}}$ -profiles and force curves to the corresponding goal data. The force responses are again perfectly reproduced, see
 380 Figure 12 (right). Linear profiles for the elasticity parameters obviously have no effect, which can be considered reasonable due to the negligible volume ratio of $\approx 0.37\%$ occupied by the interphases. On the other hand, the normalized inter-particle strain profiles are now much closer to their respective goals ($\Delta = 0.093$)
 385 and more separated from each other than before. Still, both $\tilde{\varepsilon}^{\text{NP}}$ -curves remain straight and independent of the overall strain. Furthermore, they are not able to simultaneously reproduce both goal data, at least on average. Marginal improvements can be achieved in this regard when more complex, nonlinear profiles for the elasticity parameters are considered for the interphases, but the required
 390 dependence on the overall strain cannot be realized. Altogether, this implies that the current assumption of a purely elastic material is still too simple.

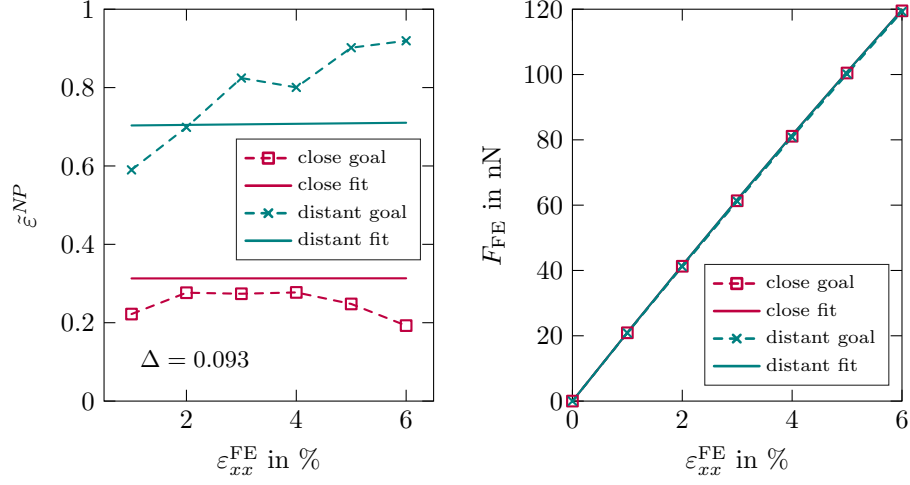


Figure 12: FE simulation results vs. Capriccio data for the close and distant cases with optimized linear profiles of the elasticity parameters inside the interphases: Profiles of normalized interparticle strain (left) and overall force (right).

3.4. Elastoplastic material with linear property profiles inside the interphases

The constitutive treatment of bulk and interphase polymer is now extended by a standard von Mises plasticity formulation with linear isotropic hardening as
 395 natively available in Abaqus. To this end, a yield stress σ^y needs to be specified. For the bulk polymer, a value of $\sigma_0^y = 50.6$ MPa has been identified from MD simulations of our model polystyrene under uniaxial tension [83]. A linear
 hardening can then be realized in Abaqus by simply prescribing the relation between plastic strains and stresses in the following tabular format, each for the
 400 bulk polymer and the four interphase layers,

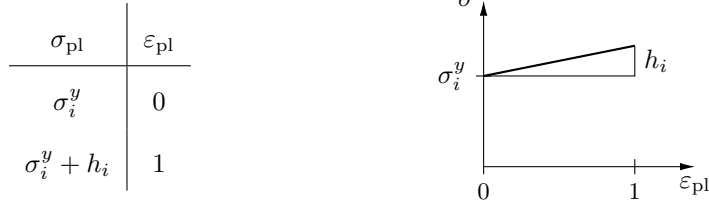


Figure 13: Realization of plastic hardening in Abaqus: Relation between plastic strains ε_{pl} and stresses σ_{pl} for each interface layer $i = 1, \dots, 4$.

i.e. for $i = 0, 1, \dots, 4$ and whereby the hardening coefficients h_i determine the slopes of the plastic yield curves (cf. Figure 13). In fact, a hyperelastoplastic approach of this form is not fully adequate for polystyrene. A hyperelastic-viscoplastic material law would be more realistic instead. However, due to the
405 current lack of rate dependence in the Capriccio data, such a formulation cannot be calibrated appropriately yet and will therefore be treated in a subsequent contribution. The preliminary limitation to simple elastoplasticity nevertheless provides new and crucial insights to explain the mechanical interphase properties and thus understand nanocomposites' behavior, as the following results
410 demonstrate.

Like in the previous subsection, linear profiles for the elasticity and plasticity parameters throughout the interphases are now to be optimized. The yield stress of the bulk polymer is thereby kept fixed at the above mentioned value. Different to this, the hardening coefficient h_0 cannot yet be derived directly from bulk
415 MD simulations, due to the limited strain range available. Therefore, the bulk hardening coefficient h_0 is left to optimization which provides

$$h_0 = 0.3269 \text{ MPa}, \quad (6)$$

i.e. a value only slightly off ideal plasticity. Furthermore, the optimizer has to determine the four slopes for E , ν , σ^y and h , which leads to the following increases relative to the bulk values, whereby also a reduction of the material

420 parameters would have been possible:

$$E_4 = 8.32406 \cdot E_0 = 7015.15 \text{ MPa} \quad (7)$$

$$\nu_4 = 1.56253 \cdot \nu_0 = 0.469 \quad (8)$$

$$\sigma_4^y = 2.28587 \cdot \sigma_0^y = 115.67 \text{ MPa} \quad (9)$$

$$h_4 = 21.4272 \cdot h_0 = 7.01 \text{ MPa} \quad (10)$$

Figure 14 compares the resulting ε^{NP} -profiles and force curves to the goal data. The linear force responses are again perfectly reproduced (cf. Figure 14 (right)), although plastic deformations are now possible everywhere in the polymer, but obviously, arise only in a volume fraction small enough not to contribute significantly. The interparticle strain profiles are reproduced very well now, including the required dependence on the overall strain resulting in $\Delta = 0.050$. Still, some improvement is desirable, but considering plasticity in the material model is essential to capture the interparticle polymer's deformation.

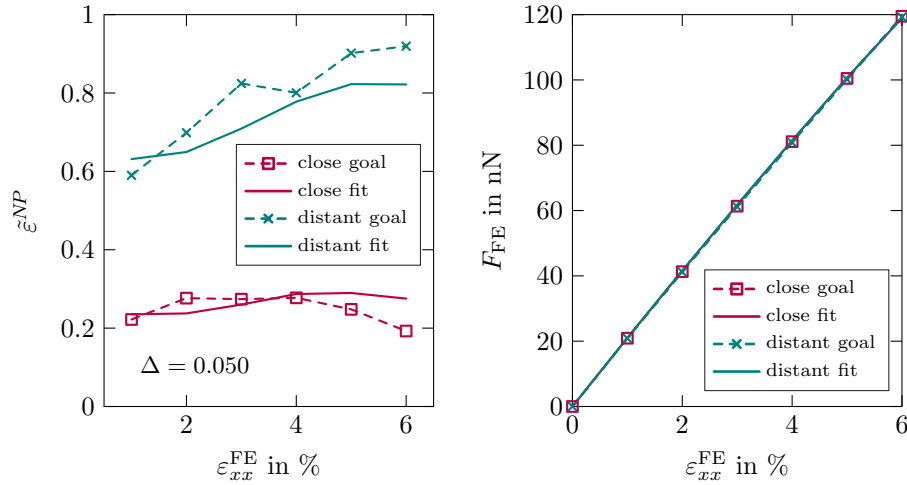


Figure 14: FE simulation results vs. Capriccio data for the close and distant cases with optimized linear profiles of the elastoplastic parameters inside the interphases: Profiles of normalized interparticle strain (left) and overall force (right).

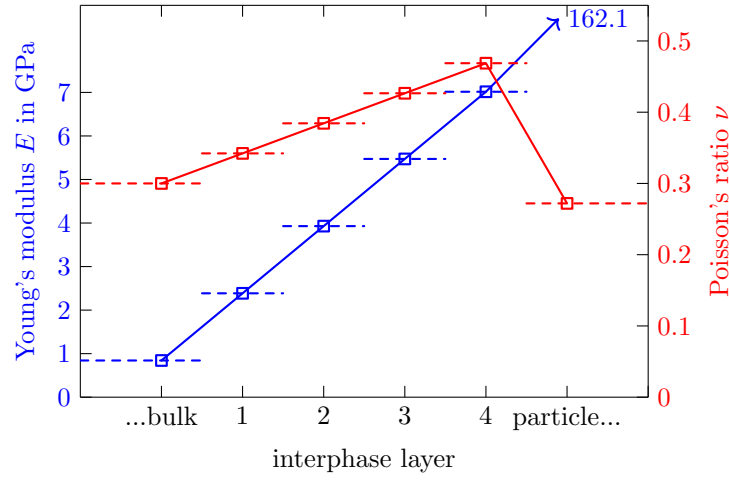


Figure 15: Optimal linear profiles for the elasticity parameters inside the interphases.

430

Figures 15 and 16 depict the corresponding linear profiles of E and ν respectively σ^y and h inside the four interphase layers. The increases in stiffness and Poisson's ratio are comparable to the hyperelastic case, whereby the former is considerably more pronounced now. Also, the optimized yield stresses and the hardening coefficients reveal significant increases towards the particle, i.e. the

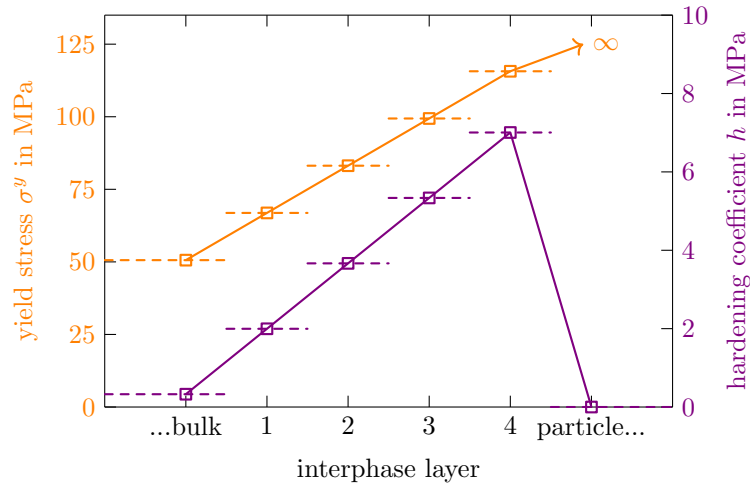


Figure 16: Optimal linear profiles for the plasticity parameters inside the interphases.

polymer is not only stiffer at the surface but also more resilient to inelastic deformations. This is an intriguing result concerning the frequently observed increase in material strength through the addition of nanofillers. A drastically increased yield point at the particle surface may very well explain the deceleration or even stop of crack propagation there.

Figure 17 contains contour plots of the equivalent plastic strain distributions around the particles and at maximum overall deformation for the close and distant cases. The volume fraction of plastically strained material is very small, which explains the apparently elastic overall responses in Figure 14. The region most strained with about a 23 % peak turns out to be the bulk polymer *between the particles* in the distant case, whereas only about one-half of this strain level is reached by the bulk *outside the particles* in the close case. The plastic zones naturally form in the tensile direction but are shielded by the particle and the surrounding, significantly stiffer and stronger interphase layers, effectively impeding potential crack propagation.

Finally, to provide better visualization of how the material properties change between the different interphase layers, one-dimensional stress-strain responses according to the different material parameter sets are depicted in Figure 18. Starting from the rather soft and nearly ideal elastoplastic curve of the bulk

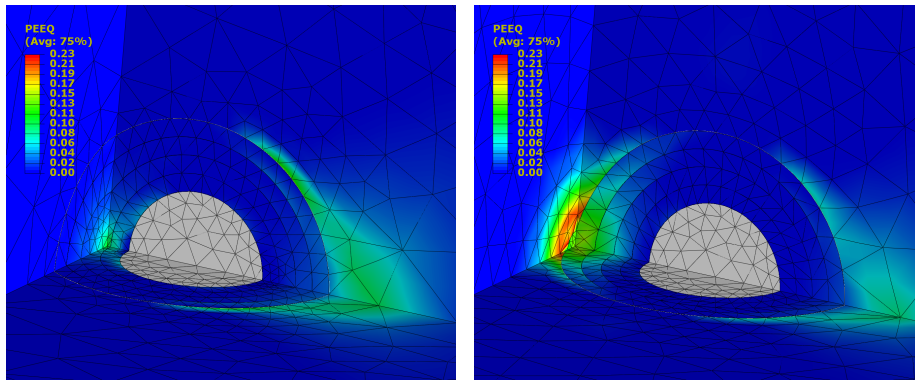


Figure 17: Equivalent plastic strain distributions around the particles at maximum overall strain $\epsilon^{FE} = 6\%$ for the close (left) and distant (right) situation.

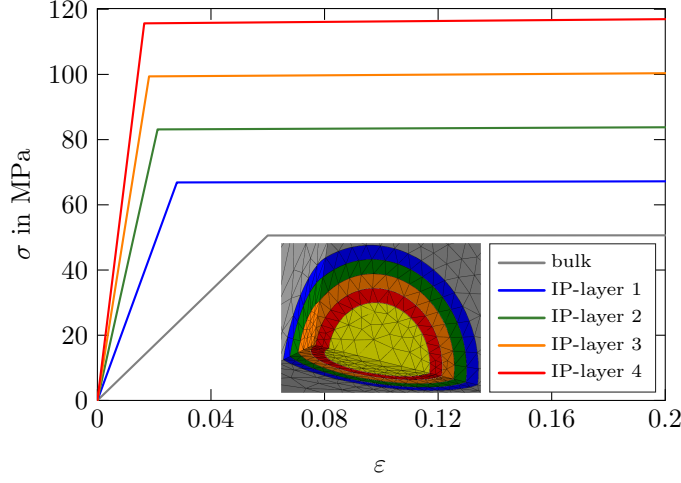


Figure 18: One-dimensional stress-strain curves for bulk polymer and the four interphase layers as resulting from the optimization of elastoplastic material behavior with linear property gradients.

polymer at the bottom, stiffness and yield stress clearly increase for the layers
 455 closer to the particle surface, whereas the hardening behavior remains more or
 less unaffected, at least in the eye-ball norm.

3.5. Elastoplastic material with exponential saturation profiles

For this final optimization, all previously linear property profiles, except
 that for Poisson's ratio ν , are now replaced by exponential saturation func-
 460 tions, which is inspired by natural growth processes. Elasticity parameters and
 yield stress of the bulk are identical to the previous values, while its hardening
 coefficient h_0 is again left to optimization, which provides

$$h_0 = 3.53385 \text{ MPa}, \quad (11)$$

i.e. a value about ten times higher than before, but still rather small compared
 to the yield stress. The material parameters E_i , σ_i^y and h_i for the different
 465 interphase layers $i = 1, \dots, 4$ are simultaneously optimized according to an ex-
 ponential saturation function of the format

$$x_i = x_0 + \frac{\alpha_x x_0}{1 + e^{5 - \beta_x i}} \quad , \quad i = 1, \dots, 4, \quad x = E, \sigma^y, h. \quad (12)$$

Hence, the interphase parameters grow exponentially towards the particle, from the bulk value as the lower bound to a multiple α_x of this as the upper saturation value, whereby the 'velocity' of this transition is governed by another parameter β_x . Together with h_0 and the slope of the linear increase of ν , eight variables in total are left to the optimizer, which then provides the following results

$$E_4 = 6582.56 \text{ MPa} \quad \text{with} \quad \alpha_E = 6.81224, \beta_E = 3.35703 \quad (13)$$

$$\nu_4 = 0.998806 \cdot \nu_0 = 0.299642 \approx \nu_0 \quad (14)$$

$$\sigma_4^y = 170.060 \text{ MPa} \quad \text{with} \quad \alpha_{\sigma^y} = 3.36544, \beta_{\sigma^y} = 1.46362 \quad (15)$$

$$h_4 = 3.53849 \approx h_0 \quad \text{with} \quad \alpha_h = 0.06, \beta_h = 0.3 \quad (16)$$

Figures 19 and 20 depict the corresponding profiles of E and ν respectively σ^y and h in the four interphase layers. Poisson's ratio ν and hardening coefficient h show nearly constant profiles, as if the optimizer could not derive any meaningful benefit from modifying these values. Different to this, Young's modulus E quickly takes its significantly larger saturation value, whereas, the yield stress σ^y increases much slower and does not reach a true plateau value. All property increases are in ranges comparable to those of the previous linear case, and the much more sophisticated exponential saturation is obviously suited to separate

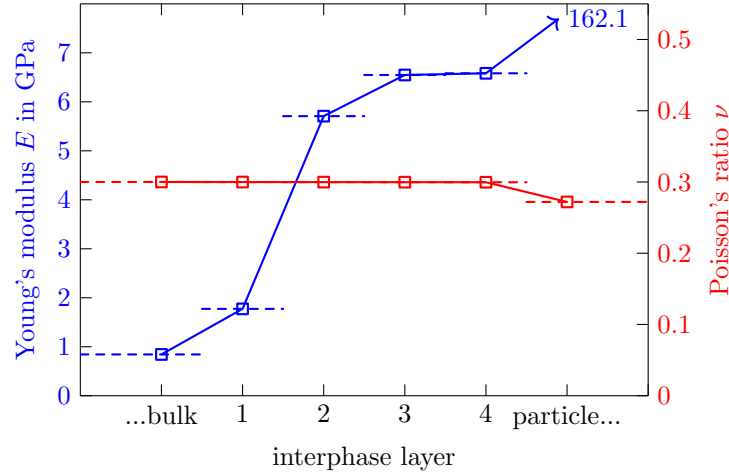


Figure 19: Optimal profiles for the elasticity parameters inside the interphases.

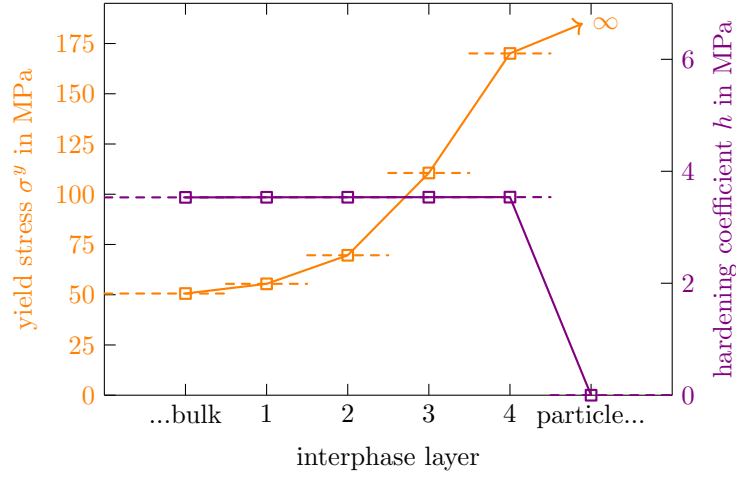


Figure 20: Optimal exponential saturation profiles for the interphase plasticity parameters.

480 the material parameters into important (E, σ^y) and less relevant (ν, h) for the different deformation characteristics of the polymer between close or distant particles. The one-dimensional elastoplastic stress-strain responses of the four interphase layers in Figure 21 provide another visualization of the property changes and emphasize the nonlinearity of the optimal parameter profiles.

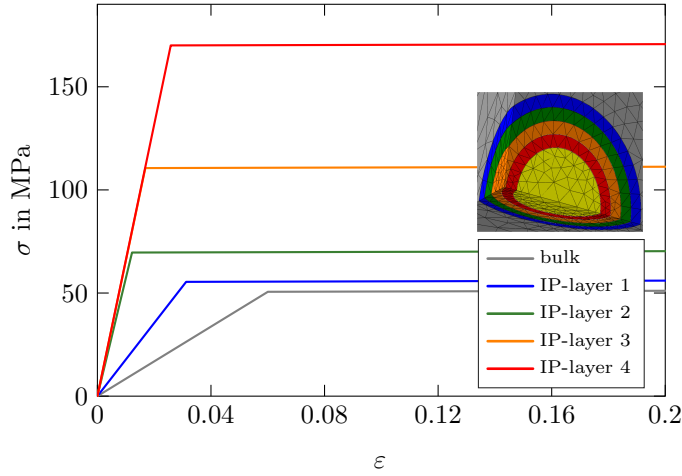


Figure 21: One-dimensional stress-strain curves for elastoplastic material with exponentially saturating profiles.

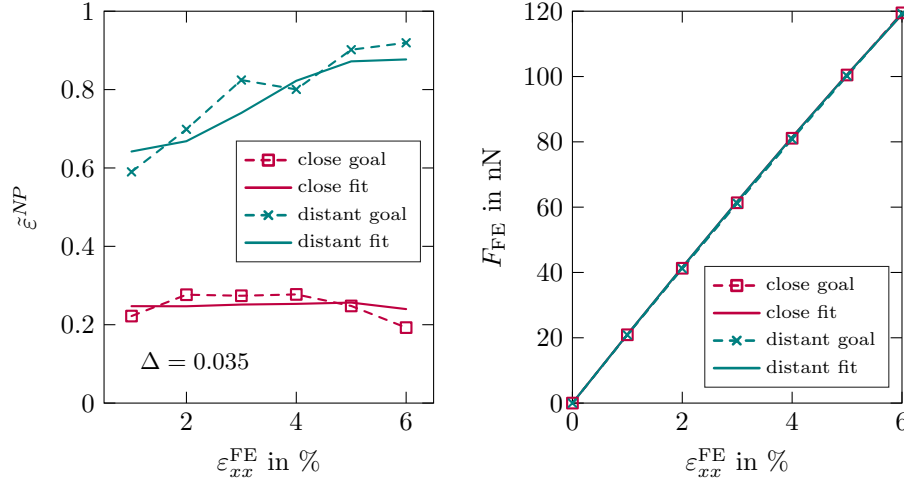


Figure 22: FE simulation results vs. Capriccio data for the close and distant cases with optimized exponential saturation profiles of the elastoplastic parameters inside the interphases: Profiles of normalized interparticle strain (left) and overall force (right).

Figure 22 finally compares the resulting $\tilde{\epsilon}^{NP}$ -profiles and force curves to the goal data. The linear force responses are still perfectly reproduced, and also the normalized interparticle strain profiles fit extremely well now with $\Delta = 0.035$ which is only a tenth of the initial $\Delta = 0.353$ obtained without interphases (cf. Figure 10).

4. Conclusions

This contribution introduces a method to numerically determine mechanical property profiles inside polymeric interphases in nanocomposites. To this end, we employ the CAPRICCIO method – a concurrent atomistic-to-continuum coupling technique – to perform MD-FE pseudo-experiments. We apply uniaxial tension to particularly designed specimens consisting of a model polystyrene matrix surrounding two silica nanoparticles at various initial distances. The normalized interparticle strain $\tilde{\epsilon}^{NP}$, which quantifies how strong the particles are bound to each other by the polymer in between them, proves to be a well-

suited measure to determine elastic and inelastic mechanical property profiles in
the vicinity of the particles. To this end, a classical inverse parameter identifi-
cation scheme based on pure FE surrogate models of the pseudo-experiments is
carried out. Here, we select a close and distant particle setting as suitable rep-
resentatives for slightly and strongly overlapping interphases. The interphases
themselves are modeled by 4 layers of equal thickness with individual material
parameters.

It turns out that a purely elastic material description is not sufficient to repro-
duce the pseudo-experimental data. Instead, an elastoplastic constitutive law
is required where exponential saturation profiles for the material parameters
deliver the best results. Interestingly, stiffness and yield stress are playing the
dominant role, whereas Poisson’s ratio and the hardening behavior are less im-
portant and remain constant within the interphase. The most impressive result
is that even an apparently linear elastic behavior requires elastoplasticity and
gradients of the particles’ plasticity parameters. This can provide entirely new
options to explain the differences in the failure behavior of nano- and microcom-
posites. In this regard, our unconventional approach can be used as a toolbox
to get insights into regions that are not accessible by experiments.

Extensions of the here presented method could investigate cross-linking poly-
mers at flat surfaces to generate comparable results for adhesion applications.
Furthermore, a homogenization of the interphase profiles determined with our
method is indispensable to enable proper structure simulations of real nanocom-
posite volumes.

Acknowledgments

In memory of our dear friend Michael C. Böhm, whose continuous enthusiasm
and support in numerous fruitful discussions is sorely missed.

525 Funding

Sebastian Pfaller is funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) - 396414850 (Individual Research Grant 'Identifikation von Interphaseneigenschaften in Nanokompositen').

530 Maximilian Ries, Paul Steinmann, and Sebastian Pfaller are funded by the DFG - 377472739 (Research Training Group GRK 2423 'Fracture across Scales - FRASCAL').

References

- [1] W. Possart, J. K. Krüger, C. Wehlack, U. Müller, C. Petersen, R. Bactavatchalou, A. Meiser, Formation and structure of epoxy network interphases at the contact to native metal surfaces, *Comptes Rendus Chimie* 9 (1) (2006) 60–79. doi:10.1016/j.crci.2005.04.009.
- [2] J. Bouchet, A.-A. Roche, The formation of epoxy/metal interphases: mechanisms and their role in practical adhesion, *The Journal of Adhesion* 78 (9) (2002) 799–830.
- 540 [3] G. Possart, M. Presser, S. Passlack, P. Geiß, M. Kopnarski, A. Brodyanski, P. Steinmann, Micro–macro characterisation of DGEBA-based epoxies as a preliminary to polymer interphase modelling, *International Journal of Adhesion and Adhesives* 29 (5) (2009) 478–487. doi:10.1016/j.ijadhadh.2008.10.001.
- 545 [4] S. Passlack, A. Brodyanski, W. Bock, M. Kopnarski, M. Presser, P. L. Geiß, G. Possart, P. Steinmann, Chemical and structural characterisation of DGEBA-based epoxies by time of flight secondary ion mass spectrometry (ToF-SIMS) as a preliminary to polymer interphase characterisation, *Analytical and Bioanalytical Chemistry* 393 (8) (2009) 1879–1888. doi:10.1007/s00216-009-2639-6.
- 550 [5] J. Batal, Charakterisierung der mechanischen Grenzschicht in Polymer-Metall-Klebungen, Ph.D. thesis (2012).

- [6] A. Meiser, Vernetzung und Alterung eines Epoxidklebstoffs im Kontakt mit Atmosphären und Metallen, Ph.D. thesis (2009).
- 555 [7] D. Fata, C. Bockenheimer, W. Possart, Epoxies on stainless steel - curing and aging, in: Adhesion, Wiley-VCH Verlag GmbH & Co. KGaA, 2006, pp. 479–505. doi:10.1002/3527607307.ch30.
- [8] J. Kanzow, F. Faupel, W. Egger, P. Sperr, G. Kögel, C. Wehlack, A. Meiser, W. Possart, Depth-resolved analysis of the aging behavior of epoxy thin
560 films by positron spectroscopy, Adhesion-Current Research and Applications, Wiley-VCH, Weinheim (2005) 465–477.
- [9] A. Meiser, K. Willstrand, P. Fehling, W. Possart, Chemical aging in epoxies: A local study of the interphases to air and to metals, The Journal of Adhesion 84 (4) (2008) 299–321. doi:10.1080/00218460802004360.
- 565 [10] A. Meiser, W. Possart, Epoxy-metal interphases: Chemical and mechanical aging, The Journal of Adhesion 87 (4) (2011) 313–330. doi:10.1080/00218464.2011.562105.
- [11] P. Vollenberg, D. Heikens, Particle size dependence of the young’s modulus of filled polymers: 1. preliminary experiments, Polymer 30 (9) (1989) 1656–
570 1662.
- [12] J. Cho, M. Joshi, C. Sun, Effect of inclusion size on mechanical properties of polymeric composites with micro and nano particles, Composites Science and Technology 66 (13) (2006) 1941–1952. doi:10.1016/j.compscitech.2005.12.028.
- 575 [13] G. Possart, P. Steinmann, Mechanical interphases in adhesive joints: Characterisation methods and fe-simulations, Adhesive Joints: Ageing and Durability of Epoxies and Polyurethanes (2018) 79–133.
- [14] A. P. Holt, P. J. Griffin, V. Bocharova, A. L. Agapov, A. E. Imel, M. D. Dadmun, J. R. Sangoro, A. P. Sokolov, Dynamics at the poly-

- mer/nanoparticle interface in poly (2-vinylpyridine)/silica nanocomposites,
Macromolecules 47 (5) (2014) 1837–1843.
- [15] A. P. Holt, V. Bocharova, S. Cheng, A. M. Kisluk, B. T. White, T. Saito,
D. Uhrig, J. P. Mahalik, R. Kumar, A. E. Imel, et al., Controlling inter-
facial dynamics: covalent bonding versus physical adsorption in polymer
nanocomposites, ACS nano 10 (7) (2016) 6843–6852.
- [16] N. Ismail, A. Ismail, A. Mustafa, T. Matsuura, T. Soga, K. Nagata,
T. Asaka, Qualitative and quantitative analysis of intercalated and ex-
foliated silicate layers in asymmetric polyethersulfone/cloisite15a® mixed
matrix membrane for co₂/ch₄ separation, Chemical Engineering Journal
268 (2015) 371–383.
- [17] D. Zhao, S. Ge, E. Senses, P. Akcora, J. Jestin, S. K. Kumar, Role of filler
shape and connectivity on the viscoelastic behavior in polymer nanocom-
posites, Macromolecules 48 (15) (2015) 5433–5438.
- [18] S. Maghami, M. Shahrooz, A. Mehrabani-Zeinabad, B. Zornoza,
M. Sadeghi, Characterization of the polymer/particle interphase in com-
posite materials by molecular probing, Polymer 205 (2020) 122792.
- [19] S. Cheng, S.-J. Xie, J.-M. Y. Carrillo, B. Carroll, H. Martin, P.-F. Cao,
M. D. Dadmun, B. G. Sumpter, V. N. Novikov, K. S. Schweizer, et al., Big
effect of small nanoparticles: a shift in paradigm for polymer nanocompos-
ites, ACS nano 11 (1) (2017) 752–759.
- [20] M. Philipp, U. Müller, R. Sanctuary, P. Seck, J.-K. Krüger, Scanning bril-
louin microscopy: acoustic microscopy at gigahertz frequencies, Archives
des Sciences Naturelles, Physiques et Mathématiques (Special volume (in-
vited Review Article)).
- [21] J.-K. Krüger, W. Possart, R. Bactavachalou, U. Müller, T. Britz, R. Sanc-
tuary, P. Alnot, Gradient of the mechanical modulus in glass–epoxy–metal

joints as measured by brillouin microscopy, *The Journal of Adhesion* 80 (7) (2004) 585–599.

- [22] R. Sanctuary, R. Bactavatchalou, U. Müller, W. Possart, P. Alnot, J.-K. Krüger, Acoustic profilometry within polymers as performed by brillouin microscopy, *Journal of Physics D: Applied Physics* 36 (21) (2003) 2738.
- [23] D. Zhao, D. Schneider, G. Fytas, S. K. Kumar, Controlling the thermo-mechanical behavior of nanoparticle/polymer films, *Acs Nano* 8 (8) (2014) 8163–8173.
- [24] E. Alonso-Redondo, L. Belliard, K. Rolle, B. Graczykowski, W. Tremel, B. Djafari-Rouhani, G. Fytas, Robustness of elastic properties in polymer nanocomposite films examined over the full volume fraction range, *Scientific reports* 8 (1) (2018) 1–8.
- [25] V. Bocharova, A.-C. Genix, J.-M. Y. Carrillo, R. Kumar, B. Carroll, A. Erwin, D. Voylov, A. Kisliuk, Y. Wang, B. G. Sumpter, et al., Addition of short polymer chains mechanically reinforces glassy poly (2-vinylpyridine)–silica nanoparticle nanocomposites, *ACS Applied Nano Materials* 3 (4) (2020) 3427–3438.
- [26] A. P. Holt, V. Bocharova, S. Cheng, A. M. Kisliuk, G. Ehlers, E. Mamonov, V. N. Novikov, A. P. Sokolov, Interplay between local dynamics and mechanical reinforcement in glassy polymer nanocomposites, *Physical Review Materials* 1 (6) (2017) 062601.
- [27] C. Huang, W. Lou, C. Tsai, T.-C. Wu, H.-Y. Lin, Mechanical properties of polymer thin film measured by the bulge test, *Thin Solid Films* 515 (18) (2007) 7222–7226.
- [28] A. Hashemi, N. Jouault, G. A. Williams, D. Zhao, K. J. Cheng, J. W. Kysar, Z. Guan, S. K. Kumar, Enhanced glassy state mechanical properties of polymer nanocomposites via supramolecular interactions, *Nano letters* 15 (8) (2015) 5465–5471.

- 635 [29] D. Maillard, S. K. Kumar, B. Fragneaud, J. W. Kysar, A. Rungta, B. C. Benicewicz, H. Deng, L. C. Brinson, J. F. Douglas, Mechanical properties of thin glassy polymer films filled with spherical polymer-grafted nanoparticles, *Nano letters* 12 (8) (2012) 3909–3914.
- [30] J. Leidner, R. Woodhams, The strength of polymeric composites containing
640 spherical fillers, *Journal of Applied Polymer Science* 18 (6) (1974) 1639–1654.
- [31] B. Pukanszky, Influence of interface interaction on the ultimate tensile properties of polymer composites, *Composites* 21 (3) (1990) 255–262.
- [32] Y. Zare, Modeling the strength and thickness of the interphase in polymer nanocomposite reinforced with spherical nanoparticles by a coupling
645 methodology, *Journal of colloid and interface science* 465 (2016) 342–346.
- [33] M. A. Ashraf, W. Peng, Y. Zare, K. Y. Rhee, Effects of size and aggregation/agglomeration of nanoparticles on the interfacial/interphase properties and tensile strength of polymer nanocomposites, *Nanoscale research*
650 *letters* 13 (1) (2018) 1–7.
- [34] W. Peng, S. Rhim, Y. Zare, K. Y. Rhee, Effect of “z” factor for strength of interphase layers on the tensile strength of polymer nanocomposites, *Polymer Composites* 40 (3) (2019) 1117–1122.
- [35] Y. Zare, A simple technique for determination of interphase properties in
655 polymer nanocomposites reinforced with spherical nanoparticles, *Polymer* 72 (2015) 93–97.
- [36] S. Chopra, K. A. Deshmukh, D. Peshwe, Theoretical prediction of interfacial properties of pbt/cnt nanocomposites and its experimental evaluation, *Mechanics of Materials* 109 (2017) 11–17.
- 660 [37] Y. Zare, The roles of nanoparticles accumulation and interphase properties in properties of polymer particulate nanocomposites by a multi-step

methodology, *Composites Part A: Applied Science and Manufacturing* 91 (2016) 127–132.

- 665 [38] Y. Zare, Development of halpin-tsai model for polymer nanocomposites assuming interphase properties and nanofiller size, *Polymer Testing* 51 (2016) 69–73.
- [39] X. L. Ji, J. K. Jing, W. Jiang, B. Z. Jiang, Tensile modulus of polymer nanocomposites, *Polymer Engineering & Science* 42 (5) (2002) 983–993.
- 670 [40] Y. Zare, Modeling approach for tensile strength of interphase layers in polymer nanocomposites, *Journal of Colloid and Interface Science* 471 (2016) 89–93. doi:10.1016/j.jcis.2016.03.029.
- [41] Y. Zare, K. Y. Rhee, A modeling approach for young’s modulus of interphase layers in polymer nanocomposites, *Physical Mesomechanics* 23 (2) (2020) 176–181. doi:10.1134/s1029959920020095.
- 675 [42] F. Zaïri, J.-M. Gloaguen, M. Naït-Abdelaziz, A. Mesbah, J.-M. Lefebvre, Study of the effect of size and clay structural parameters on the yield and post-yield response of polymer/clay nanocomposites via a multiscale micromechanical modelling, *Acta Materialia* 59 (10) (2011) 3851–3863.
- 680 [43] Y. Zare, K. Y. Rhee, D. Hui, Influences of nanoparticles aggregation/agglomeration on the interfacial/interphase and tensile properties of nanocomposites, *Composites Part B: Engineering* 122 (2017) 41–46. doi:10.1016/j.compositesb.2017.04.008.
- [44] Y. Zare, Study of nanoparticles aggregation/agglomeration in polymer particulate nanocomposites by mechanical properties, *Composites Part A: Applied Science and Manufacturing* 84 (2016) 158–164. doi:10.1016/j.compositesa.2016.01.020.
- 685 [45] S. A. Shandiz, A. Montazeri, A novel MD-based procedure to obtain the interphase young’s modulus in nanocomposites, *Computational Materials Science* 113 (2016) 104–111. doi:10.1016/j.commatsci.2015.11.036.

- 690 [46] G. M. Odegard, T. S. Gates, L. M. Nicholson, K. E. Wise,
Equivalent-continuum modeling of nano-structured materials, Com-
posites Science and Technology 62 (14) (2002) 1869 – 1880.
doi:[http://dx.doi.org/10.1016/S0266-3538\(02\)00113-6](http://dx.doi.org/10.1016/S0266-3538(02)00113-6).
URL [http://www.sciencedirect.com/science/article/pii/](http://www.sciencedirect.com/science/article/pii/S0266353802001136)
695 [S0266353802001136](http://www.sciencedirect.com/science/article/pii/S0266353802001136)
- [47] G. Odegard, T. Clancy, T. Gates, Modeling of the mechanical properties
of nanoparticle/polymer composites, Polymer 46 (2) (2005) 553 – 562.
doi:<http://dx.doi.org/10.1016/j.polymer.2004.11.022>.
URL [http://www.sciencedirect.com/science/article/pii/](http://www.sciencedirect.com/science/article/pii/S0032386104011243)
700 [S0032386104011243](http://www.sciencedirect.com/science/article/pii/S0032386104011243)
- [48] E. B. Tadmor, R. E. Miller, Modeling materials: continuum, atomistic and
multiscale techniques, Cambridge University Press, 2011.
- [49] R. Smit, W. Brekelmans, H. Meijer, Prediction of the mechanical behavior
of nonlinear heterogeneous systems by multi-level finite element modeling,
705 Computer Methods in Applied Mechanics and Engineering 155 (1-2) (1998)
181–192. doi:[10.1016/S0045-7825\(97\)00139-4](http://dx.doi.org/10.1016/S0045-7825(97)00139-4).
- [50] F. Feyel, Multiscale FE² elastoviscoplastic analysis of composite struc-
tures, Computational Materials Science 16 (1-4) (1999) 344–354.
doi:[http://dx.doi.org/10.1016/S0927-0256\(99\)00077-4](http://dx.doi.org/10.1016/S0927-0256(99)00077-4).
710 URL [http://www.sciencedirect.com/science/article/pii/](http://www.sciencedirect.com/science/article/pii/S0927025699000774)
[S0927025699000774](http://www.sciencedirect.com/science/article/pii/S0927025699000774)
- [51] P. Kumar, P. Steinmann, J. Mergheim, Enhanced computational homoge-
nization techniques for modelling size effects in polymer composite, Com-
putational Mechanics, in submission.
- 715 [52] E. B. Tadmor, M. Ortiz, R. Phillips, Quasicontinuum analysis of defects in
solids, Philosophical Magazine A 73 (6) (1996) 1529–1563. arXiv:[http://](http://www.tandfonline.com/doi/pdf/10.1080/01418619608243000)
www.tandfonline.com/doi/pdf/10.1080/01418619608243000, doi:[10.1080/01418619608243000](http://dx.doi.org/10.1080/01418619608243000).

- [53] E. B. Tadmor, The Quasicontinuum method, Ph.D. thesis, Brown University (1996).
720
- [54] H. Ben Dhia, G. Rateau, The Arlequin method as a flexible engineering design tool, *International Journal for Numerical Methods in Engineering* 62 (11) (2005) 1442–1462. doi:10.1002/nme.1229.
- [55] H. Ben Dhia, N. Elkhodja, F. X. Roux, Multimodeling of multi-
725 altered structures in the Arlequin framework. solution with a domain-decomposition solver, *European Journal of Computational Mechanics* 17 (2008) 969–980.
- [56] T. Belytschko, S. P. Xiao, Coupling methods for continuum model with molecular model, *International Journal for Multiscale Computational Engineering* 1 (2003) 115–126.
730
- [57] P.-A. Guidault, T. Belytschko, On the l^2 and h^1 couplings for an overlapping domain decomposition method using lagrange multipliers, *International Journal for Numerical Methods in Engineering* 70 (3) (2007) 322–350. doi:10.1002/nme.1882.
- [58] M. Rahimi, H. A. Karimi-Varzaneh, M. C. Böhm, F. Müller-Plathe,
735 S. Pfaller, G. Possart, P. Steinmann, Nonperiodic stochastic boundary conditions for molecular dynamics simulations of materials embedded into a continuum mechanics domain, *Journal of Chemical Physics* 134 (2011) 154108.
- [59] S. Pfaller, G. Possart, P. Steinmann, M. Rahimi, F. Müller-Plathe, M. C. Böhm, A comparison of staggered solution schemes for coupled particle-
740 continuum systems modeled with the Arlequin method, *Computational Mechanics* 49 (5) (2012) 565–579. doi:10.1007/s00466-011-0657-7.
URL <http://dx.doi.org/10.1007/s00466-011-0657-7>
- [60] S. Pfaller, M. Rahimi, G. Possart, P. Steinmann, F. Müller-Plathe,
745 M. Böhm, An Arlequin-based method to couple molecular dynamics and

- finite element simulations of amorphous polymers and nanocomposites, Computer Methods in Applied Mechanics and Engineering 260 (0) (2013) 109–129. doi:<http://dx.doi.org/10.1016/j.cma.2013.03.006>.
- 750 URL <http://www.sciencedirect.com/science/article/pii/S0045782513000571>
- [61] S. Pfaller, Multiscale simulation of polymers, Ph.D. thesis, Friedrich-Alexander-Universität Erlangen-Nürnberg (2015).
- [62] S. Pfaller, A. Kergaßner, P. Steinmann, Optimisation of the Capriccio
755 Method to Couple Particle- and Continuum-Based Simulations of Polymers, Multiscale Science and Engineering 1 (4) (2019) 318–333. doi:
10.1007/s42493-019-00028-y.
URL <https://doi.org/10.1007/s42493-019-00028-y>
- [63] W. Zhao, P. Steinmann, S. Pfaller, A particle-continuum coupling method
760 for multiscale simulations of viscoelasticviscoplastic amorphous glassy polymers, in preparation.
- [64] M. Ries, P. Steinmann, S. Pfaller, The hybrid capriccio method: A 1d study for further advancement, Proceedings of World Congress on Computational Mechanics, submitted.
- 765 [65] I. Chung, M. Cho, Recent studies on the multiscale analysis of polymer nanocomposites, Multiscale Science and Engineering 1 (3) (2019) 167–195.
- [66] F. Ebrahimi, A. Dabbagh, A comprehensive review on modeling of nanocomposite materials and structures, Journal of Computational Applied Mechanics 50 (1) (2019) 197–209.
- 770 [67] E. Van Der Giessen, P. A. Schultz, N. Bertin, V. V. Bulatov, W. Cai, G. Csányi, S. M. Foiles, M. G. Geers, C. González, M. Hütter, et al., Roadmap on multiscale materials modeling, Modelling and Simulation in Materials Science and Engineering 28 (4) (2020) 043001.

- [68] S. Pfaller, G. Possart, P. Steinmann, M. Rahimi, F. Müller-Plathe,
775 M. Böhm, Investigation of interphase effects in silica-polystyrene nanocomposites based on a hybrid molecular-dynamics-finite-element simulation framework, *Physical Review E* 93 (5) (2016) 052505.
URL <http://dx.doi.org/10.1103/PhysRevE.93.052505>
- [69] H. Ben Dhia, Problèmes mécaniques multi-échelles: la méthode Arlequin,
780 *Comptes Rendus de l'Académie des Science, Series II b* 326 (1998) 899–904.
- [70] P. T. Bauman, H. Ben Dhia, N. Elkhodja, J. T. Oden, S. Prudhomme, On the application of the Arlequin method to the coupling of particle and continuum models, *Computational Mechanics* 42 (4) (2008) 511–530. doi: 10.1007/s00466-008-0291-1.
- [71] M. Ries, G. Possart, P. Steinmann, S. Pfaller, Extensive CGMD Simulations of Atactic PS Providing Pseudo Experimental Data to Calibrate Nonlinear Inelastic Continuum Mechanical Constitutive Laws, *Polymers* 11 (11) (2019) 1824.
- [72] M. Ries, P. Steinmann, S. Pfaller, Characterization of polystyrene under
790 shear deformation using molecular dynamics, in: *Developments and Novel Approaches in Nonlinear Solid Body Mechanics*, Springer International Publishing, 2020, pp. 219–229. doi:10.1007/978-3-030-50460-1_14.
- [73] M. Ries, F. Weber, M. Striegel, P. Steinmann, S. Pfaller, Multiscale femd coupling: Influence of the chain length on the mechanical behavior of
795 coarse-grained polystyrene, *Proceedings of World Congress on Computational Mechanics*, submitted.
- [74] W. Zhao, M. Ries, P. Steinmann, S. Pfaller, A viscoelastic-viscoplastic constitutive model for glassy polymers based on molecular dynamics simulations under uniaxial deformation, *International Journal of Solids and Structures* (submitted).
800

- [75] A. Ghanbari, T. V. M. Nodoro, F. Leroy, M. Rahimi, M. C. Böhm, F. Müller-Plathe, Interphase structure in silica-polystyrene nanocomposites: A coarse-grained molecular dynamics study, *Macromolecules* 45 (1) (2012) 572–584. [arXiv:http://pubs.acs.org/doi/pdf/10.1021/ma202044e](http://pubs.acs.org/doi/pdf/10.1021/ma202044e), doi:10.1021/ma202044e.
URL <http://pubs.acs.org/doi/abs/10.1021/ma202044e>
- [76] D. Reith, M. Pütz, F. Müller-Plathe, Deriving effective mesoscale potentials from atomistic simulations, *Journal of Computational Chemistry* 24 (13) (2003) 1624–1636.
- [77] H. A. Karimi-Varzaneh, H.-J. Qian, X. Chen, P. Carbone, F. Müller-Plathe, IBIsCO: A molecular dynamics simulation package for coarse-grained simulation, *Journal of Computational Chemistry* 32 (2011) 1475–1487.
- [78] A. Ghanbari, M. Rahimi, J. Dehghany, Influence of surface grafted polymers on the polymer dynamics in a silica-polystyrene nanocomposite: A coarse-grained molecular dynamics investigation, *The Journal of Physical Chemistry C* 117 (47) (2013) 25069–25076. [arXiv:http://pubs.acs.org/doi/pdf/10.1021/jp407109r](http://pubs.acs.org/doi/pdf/10.1021/jp407109r), doi:10.1021/jp407109r.
URL <http://pubs.acs.org/doi/abs/10.1021/jp407109r>
- [79] T. V. Nodoro, E. Voyatzis, A. Ghanbari, D. N. Theodorou, M. C. Böhm, F. Müller-Plathe, Interface of grafted and ungrafted silica nanoparticles with a polystyrene matrix: Atomistic molecular dynamics simulations, *Macromolecules* 44 (2011) 2316–2327.
- [80] E. Riccardi, M. C. Böhm, F. Müller-Plathe, Molecular dynamics approach to locally resolve elastic constants in nanocomposites and thin films: Mechanical description of solid-soft matter interphases via young’s modulus, poisson’s ratio and shear modulus, *The European Physical Journal E* 37 (10). doi:10.1140/epje/i2014-14103-5.
URL <http://dx.doi.org/10.1140/epje/i2014-14103-5>

- [81] S. Liu, S. Pfaller, M. Rahimi, G. Possart, P. Steinmann, M. C. Böhm, F. Müller-Plathe, Uniaxial deformation of polystyrene–silica nanocomposites studied by hybrid molecular dynamics–finite element simulations, *Computational Materials Science* 129 (2017) 1 – 12. doi:<http://dx.doi.org/10.1016/j.commatsci.2016.11.031>. URL <http://www.sciencedirect.com/science/article/pii/S0927025616305924>
- [82] P. Steinmann, M. Hossain, G. Possart, Hyperelastic models for rubber-like materials: consistent tangent operators and suitability for treloar’s data, *Archive of Applied Mechanics* 82 (2012) 1183–1217.
- [83] M. Rahimi, I. Iriarte-Carretero, A. Ghanbari, M. C. Böhm, F. Müller-Plathe, Mechanical behavior and interphase structure in a silica-polystyrene nanocomposite under uniaxial deformation, *Nanotechnology* 23 (2012) 305702.