Gradient of mechanical properties in polymer nanocomposites: From atomistic scale to the strain gradient effective continuum

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Keywords: *Polymer nanocomposite, Molecular dynamic simulations, Strain gradient interphase, Hyper-stress and strain gradient, Unfolding method for homogenization, Strain gradient constitutive law*

Glassy polymer nanocomposites (PNCs) exhibit heterogeneous mechanical properties due to the presence of a distinct polymer/nanoparticle (NP) interfacial region, whose rigidity strongly influences the overall mechanical response. Classical continuum theories typically model the interphase behavior as dependent only on deformation, neglecting the strong internal deformation gradients that call for enriched continuum descriptions of PNCs. In this work, we formulate a higher-gradient elasticity constitutive law for the polymer/NP interphase via a systematic micro–meso–macro coupling informed by atomistic molecular dynamics (MD) simulations. We show that an accurate description of the polymer/NP interphase requires modeling it as a strain-gradient material, while the bulk polymer can still be treated as a Cauchy material due to significantly weaker strain-gradient effects. The interphase thickness is determined from equilibrium density profiles obtained from MD simulations. By upscaling the molecular response within the interphase, an effective strain-gradient continuum model is derived, in which stress, strain, hyperstress, and conjugate strain gradients are computed at the atomic scale. A further homogenization step, based on the unfolding method, enables identification of the strain-gradient elastic moduli, leading to a second-gradient linear elastic constitutive law for the interphase.

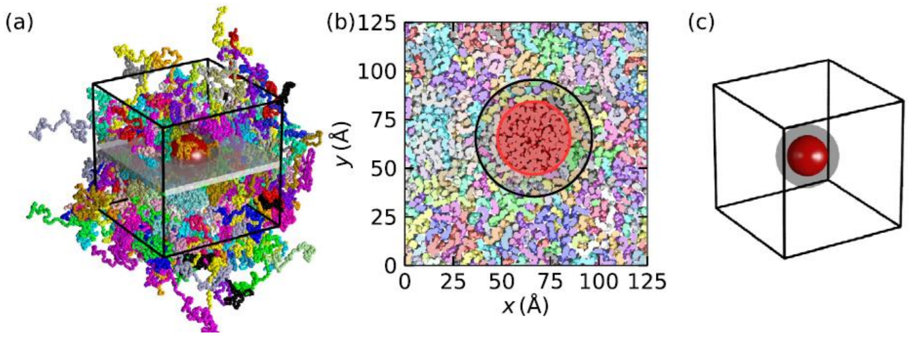

Figure 1. (a) Snapshot of the atomistic PNC model. The interphase is presented by the region between the semitransparent grey sphere and the NP. A slice of thickness 6 Å passing through the center of NP is also shown. (b) Top view of the distribution of atoms though the slice shown in (a). (c) Schematic of the equivalent continuum model employed for the strain gradient homogenized model, showing the internal structure of the NP (red) and interphase (grey). The material within the rest of the box is filled with polymer (PB) matrix.

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