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A coarse-grained model for the mechanical behavior of multi-layer graphene

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ABSTRACT

Graphene is the strongest and highest weight-to-surface ratio material known, rendering it an excellent building block for nanocomposites. Multi-layer graphene (MLG) assemblies have intriguing mechanical properties distinct from the monolayer that remain poorly understood due to spatiotemporal limitations of experimental observations and atomistic modeling. To address this issue, here we establish a coarse-grained molecular dynamics (CG-MD) model of graphene using a strain energy conservation approach. The model is able to quantitatively reproduce graphene's mechanical response in the elastic and fracture regimes. The hexagonal symmetry of graphene's honeycomb lattice is conserved, and therefore the anisotropy in the non-linear large-deformation regime between the zigzag and armchair directions is preserved. The superlubricity effect, namely the strong orientational dependence of the shear rigidity between graphene layers, is also captured. We demonstrate the applicability of the model by reproducing recent experimental nano-indentation results *in silico*. Our model overcomes the limitations of current CG-MD approaches, in accurately predicting the fracture properties, the interlayer shear response, and the intrinsic anisotropy of MLG. Additionally, our fast, transferable force-field can be straightforwardly combined with existing coarse-grained models of polymers and proteins to predict the meso-scale behavior of hybrid carbon nanomaterials.

1. Introduction

Graphene consists of a one-atom thick 2D hexagonal lattice of covalently bonded carbon atoms via sp2-orbitals [1]. Monolayer graphene exhibits remarkable electronic [2] and thermal properties [3] and it is the strongest material known [4], offering great promise for a broad range of nanotechnological applications [5]. However, harnessing the mechanical properties of the monolayer at larger length scales or for higher material hierarchies (e.g. multi-layer graphene or MLG) remains a bottleneck [6,7]. Despite the great progress made on the synthesis side of MLG in the past few years [8,9], the physical mechanisms governing their mechanical performance, which span multiple length scales [10], remain poorly understood. On the one hand, experimental techniques offer limited insight into the molecular scale processes because their resolution is limited at the nanoscale. On the other hand, large-deformation and failure mechanisms at the mesoscale are prohibitively expensive to study with full atomistic simulations.

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In order to address these scale-related issues and obtain a comprehensive physical understanding of the behavior of MLG assemblies, a computational multi-scale approach is required. In particular, coarse-grained molecular dynamics (CG-MD) models, where groups of atoms are clustered into beads that interact through an effective force-field, offer great promise as they allow simulating mesoscale physical processes while retaining the molecular detail of the system. CG-MD has been extensively employed to study a variety of problems involving graphene, such as self-assembly of graphene nanosheets in lipid membranes [11], adsorption of surfactants [12] and peptides [13] on graphene or detergent on carbon nanotubes [14], the mechanics of graphene folding [15,16] or membrane penetration of graphene microsheets [17,18]. There have been two major approaches to developing CG-MD models of graphene. The first one uses the Martini force-field developed by Marrink et al. [19]. The second approach is based on strain energy conservation between an atomistic system and the reduced order model [15]. These approaches, although perfectly suitable in the context of their studies, cannot be readily used to study the mechanical response of MLG [6,20]. First, both approaches employ harmonic covalent bonds that give rise to large errors when sheets are subject to large-deformations, for instance, in the case of typical nanoindentation experiments. Second, existing models have not been validated in their capability to capture the interlayer shear response and intrinsic anisotropic features of graphene, which are important factors that govern the performance of MLG systems. The Martini force-field has been successfully employed to simulate proteins and some polymer chemistries but it requires recalibration for describing the elastic properties of graphene [11]. The strain energy conservation approach [15] on the other hand, has been successfully applied to reproduce the linear elastic mechanical response of very large scale graphene systems. However, due to the high level of coarse-graining mapping (~250 carbon atoms to 1 CG bead), it is challenging to capture MLG or graphene-polymer nanocomposite behavior with the existing parameterizations. It would be desirable to have an experimentally validated CG model that blends the best qualities of these two distinct approaches to set the stage for large-scale studies of MLGs and nanocomposite systems.

To address this issue, we develop here a coarse-grained model of graphene that enables simulating large-deformation and failure of large-scale graphene-based hierarchical systems with a ~200 fold increase in computational speed with respect to atomistic reactive force-fields necessary to capture equivalent physical processes. The bonded interactions in our model are anharmonic and breakable, which allow to capture the non-linear response and fracture of graphene. Similarly to the Martini approach, the proposed model consists of a 4:1 mapping of atoms to CG beads, rendering it compatible with other existing CG representations of proteins or polymers. The hexagonal symmetry of the graphene lattice is conserved, making it possible to capture the anisotropic mechanical behavior in the zigzag and armchair directions for large-deformations as well as possible asymmetries in the adsorption mechanisms of macromolecules [12]. The force-field parameters of the reduced order model are calibrated using some well-known elastic and fracture mechanical properties of graphene, and the interlayer adhesion energies between graphene layers. The model, calibrated to just reproduce the interlayer adhesion, features a strong dependence of the interlayer shear stiffness with the relative orientation between the graphene layers, an effect also known as superlubricity.

In this paper, we first provide a description of the CG-MD model of graphene. Then, we present the approach used to calibrate the force-field parameters. Next, after having established the basic features of the model, we discuss its validation by testing the model performance under a variety of relevant conditions that are outside the calibration range and comparing the results with experimental evidence found in the literature. Finally, we demonstrate the applicability and predictive power of the model by simulating nanoindentation of a graphene monolayer, and the uniaxial tensile test of a graphene paper.

2. Methods

2.1. Coarse-grained model description

The CG-MD model consists of a hexagonal lattice of beads where each bead represents 4 atoms of the graphene atomistic lattice (Fig. 1a). This CG level is in line with commonly used approaches, such as Martini, where usually 3 or 4 heavy atoms are clustered in a single bead, facilitating the compatibility between our model and other existing models of polymer and protein materials [21–23]. While most CG models of graphene ignore the hexagonal symmetry of the atomistic lattice, here we show that it is needed to capture asymmetries between the zigzag and armchair directions in the non-linear large-deformation regime and in the interlayer shear response [24].

The force-field of the CG-MD model includes the contributions from bonds, angles, dihedrals and non-bonded interactions to the potential energy of the system (Fig. 1b). The total potential energy of the system can be written as:

$$E_{pot} = E_b + E_a + E_d + E_{nb} \tag{1}$$

where E_b, E_a, E_d, E_{nb} are the sum over the energies of all the bonds, angles, dihedrals, and pair-wise non-bonded interactions of the system respectively. The functional forms of the different contributions for a single interaction are the following:

$$V_b(d) = D_0[1 - e^{-\alpha(d-d_0)}]^2 \tag{2}$$

$$V_a(\theta) = k_\theta(\theta - \theta_0)^2 \tag{3}$$

$$V_d(\phi) = k_\phi[1 - \cos(2\phi)] \tag{4}$$

$$V_{nb}(r) = 4\varepsilon_{LJ}\left[\left(\frac{\sigma_{LJ}}{r}\right)^{12} - \left(\frac{\sigma_{LJ}}{r}\right)^{6}\right] \tag{5}$$

Where D_0 and α are the depth and a parameter related to the width of the potential well of the bond respectively, d_0 is the equilibrium distance of the bond, k_θ is the spring constant of the angle interaction, θ_0 is the equilibrium angle, k_ϕ is the spring constant of the dihedral interaction, ε_{LJ} is the depth of the Lennard-Jones potential well for non-bonded interactions, and σ_{LJ} is the Lennard-Jones parameter associated with