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Designing graphene structures with controlled distributions of topological defects: A case study of toughness enhancement in graphene ruga

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ABSTRACT

A novel design methodology combining phase field crystal method and atomistic simulations is proposed to solve the inverse problem of finding the optimized distribution and type of topological defects that make a graphene sheet conform to a targeted arbitrary three dimensional (3D) surface. To demonstrate potential applications of the proposed method, we created a sinusoidal graphene structure with wavelength of 4 nm and amplitude of 0.75 nm, and then demonstrated using large-scale molecular dynamics (MD) simulations that the constructed graphene ruga[1] has a fracture toughness around 25 J/m^2, which is about twice that of the defect-free graphene. The underlying toughening mechanisms include nanocrack shielding and atomic scale crack bridging. This study suggests a promising general methodology to tailor-design mechanical properties of graphene through controlled distributions of topological defects.

1. Introduction

Topological defects (such as disclinations, dislocations and grain boundaries) play a crucial role in altering the electrical properties [2–5], mechanical strength [6–14], lithium absorption [15–17], and wrinkled configurations [18–24] of graphene. It has been proposed that the collective behaviors of topological defects can be utilized to controllably design 3D graphene structures [24] to achieve specific properties and functionalities. For example, graphene structures with negative curvature have been shown to significantly enhance the capacity of graphene based electrodes [15,16]. A designed large carbon molecule capable of folding into a spherical cap can be used as a basis to control the chirality of carbon nanotubes during growth [25].

Early experiments on graphene synthesis through chemical vapor deposition (CVD) often involve randomly distributed grain boundaries and dislocations in polycrystalline samples [4]. Over the last few years, rapid developments in experimental capabilities have made it possible to increasingly control the types and positions of defects in graphene [26] or large two dimensional (2D) molecular sheets of carbon [25,27]. These progresses have paved a way to tailor-design graphene structures and are calling for more in-depth studies on mechanical and physical properties of graphene with controlled distributions of topological defects. Questions of interest include: (1) How to determine the required distribution of defects to conform

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[1] The Latin word ruga is used to refer to a large-amplitude state of wrinkle, crease, ridge or fold [1].

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graphene to a desired 3D configuration, and (2) what configuration would lead to a specific targeted property.

Despite a dramatic increase in computational power in recent years, the inverse problem of determining the required distribution of topological defects to create a specific 3D configuration or structure of graphene through existing atomistic simulations or continuum modeling techniques remains an open challenge due to the highly nonlinear nature of the problem. Previous studies have attempted to employ geometrical methods [28,29] and Monte Carlo simulations [30] to search for equilibrium positions of carbon atoms on a simple curved surface. However, it has been difficult to extend such methods to large systems with complicated geometries because of their intrinsic limitations on length and time scales. Recently, the so-called phase field crystal (PFC) method [31] has been developed to model self-organization and pattern formation in crystalline materials with over-damped conservative (diffusive) dynamics [32]. In this paper, we demonstrate that PFC and atomistic simulations can be jointly used to solve the inverse problem of finding the optimized distribution and type of topological defects that make a graphene sheet conform to a targeted arbitrary three dimensional (3D) surface, and that a sinusoidal graphene ruga [1] created via the proposed methodology can dramatically enhance the fracture toughness of graphene. It is emphasized that one of the central points of our work is to 'design' 3D graphene structures with topological defects, i.e., to solve the inverse problem of finding the defect distribution and type that lead to a targeted geometry, and to generate/create the full-atom configuration of the designed graphene structure.

2. Methods

Here we provide a brief review of the PFC method and refer the reader to the literatures for more details [31,32]. As an emerging and increasingly popular method, PFC describes the dissipative dynamics of a discrete atomic structure by using a continuum density functional with periodical solutions that can be obtained through energy minimization or by solving a diffusion equation [31]. Compared to conventional continuum and atomistic modeling approaches, it has been demonstrated that PFC not only captures the physics of atomic-scale elastoplasticity, but can also describe the diffusive dynamics of phase transformation and microstructure evolution. PFC operates on atomic length and diffusive time scales [32], and is thought to be an alternative to atomistic simulations. The free energy functional in the original PFC model follows the Swift–Hohenberg (SH) equation [31],

$$F = \int \left[\frac{\phi}{2} \left(-\epsilon + (1 + \Delta)^2 \right) \phi + \frac{1}{4} \phi^4 \right] d\mathbf{x}, \tag{1}$$

where $\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}$ is the Laplace operator in 2D, ϕ the reduced density and ϵ the reduced temperature. If the dynamics of density evolution is assumed to be dissipative, one obtains the following governing equation,

$$\frac{\partial \phi}{\partial t} = \Delta \left\{ \left(-\epsilon + (1 + \Delta)^2 \right) \phi + \phi^3 \right\}. \tag{2}$$

In the current study, we use the finite element method (FEM) to solve the above PFC equation, as FEM offers more flexibility in handling complicated geometrical shapes than spectral methods in Fourier space. The numerical scheme for solving Eq. (2) is based on a mixed formulation of FEM, with the introduction of two new variables to reduce the highest order in spatial derivative [33]. The present problem involves dynamic evolution on a 3D curved surface Γ, for which the surface Laplace operator Δ_Γ should be used in Eq. (2). Similar applications of PFC include finding the distribution of charged particles on a sphere [34] and patterns of distributed particles on a catenoid surface [35].

To implement PFC, we made use of the software platform FEniCS [36] to solve the governing equation in FEM. FEniCS is a collection of free software components for automated and efficient solutions of partial differential equations (PDE) and has been widely used to solve problems in both fluid and solid mechanics. Since the derivative operator on a curved manifold has been embedded in FEniCS, the same code can be used for both flat and curved surfaces, which significantly simplifies the coding effort.

MD simulations of graphene structures were carried out via Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [37]. Visualization is processed via software package Ovito [38]. The interatomic force is described by the adaptive intermolecular reactive empirical bond order (AIREBO) potential [39]. To avoid a non-physical post-hardening behavior known to exist for the AIREBO potential, the smaller cut-off distance in the switching function of AIREBO is taken to be 2.0 Å [9,40,41]. Atomic scale stresses were calculated via the Virial theorem, and the thickness of graphene was set to be 3.34 Å in stress calculation. This value represents the atomic thickness of single-layer graphene and is different from the effective thickness used in continuum modeling [42] of bending-dominated deformation in graphene.

3. Results

Figure 1 describes the basic methodology of using PFC to design a curved 3D graphene structure with distributed topological defects, as exemplified by a sinusoidal graphene. First, PFC is applied on the targeted curved manifold (Fig. 1(a)) to evolve an equilibrium triangular pattern of continuum density waves corresponding to a minimum energy state (Fig. 1(b)). Identifying wave crests as particles converts the triangular pattern of density waves into a discrete triangular lattice network (Fig. 1(c)), which is then transformed into a full-atom graphene structure via Voronoi construction on the triangular lattice. Finally, a thermodynamically stable structure with wavelength of 4 nm and amplitude of 0.75 nm (Fig. 1(d)) is obtained after MD equilibration at a finite temperature under the NPT ensemble. For the sinusoidal ruga structure shown in Fig. 1(d), pentagons are found at crests and valleys, while heptagons at the saddle points. This atomic structure is the same as that found in a previous study [43]. For an arbitrary curved surface, even as complex as a 3D nanoporous graphene fabricated by CVD on a metal foam [44,45], it