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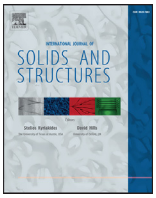

Adhesion mechanics of graphene on textured substrates

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ABSTRACT

Graphene, the two dimensional form of carbon, has excellent mechanical, electrical and thermal properties and a variety of potential applications including nano-electro-mechanical systems, protective coatings, transparent electrodes in display devices and biological applications. Adhesion plays a key role in many of these applications. In addition, it has been proposed that the electronic properties of graphene can be affected by elastic deformation caused by adhesion of graphene to its substrate. In light of this, we present here a continuum mechanics based theoretical framework to understand the effect of nanoscale morphology of substrates on adhesion and mechanics of graphene. In the first part, we analyzed the adhesion mechanics of graphene on one and two dimensional periodic corrugations. We carried out molecular statics simulations and found the results to be in good agreement with our theory. We modeled adhesive interactions as surface forces due to a Lennard–Jones 6–12 potential in both our analysis and simulations and in principle any other interaction potential can be used with our methodology. The results show that graphene adheres conformally to substrates with large curvatures. We showed in principle that the theory developed here can be extended to substrates with arbitrary textures that can be represented by a Fourier series.

In the second part, we study the mechanics of peeling of graphene ribbons from one dimensional sinusoidally textured substrates. In the molecular statics simulations, we observed two key features in the peel mechanics of the ribbons - the ribbons slide over the substrate and undergo adhesion and peeling near the crack front in an oscillatory manner, the frequency of which reveals the wavelength of the underlying substrate. Our theory qualitatively captures these features of the peel mechanics and is general enough that it can be extended to other two dimensional materials like Molybdenum Disulphide (MoS2), Boron Nitride (BN) or other thin films and different kinds of interaction potentials.

1. Introduction and background

Graphene is a two-dimensional crystalline allotrope of carbon with desirable properties (Geim, 2009; Geim and Novoselov, 2007) like high Young's modulus ($\sim$1 TPa) and mechanical strength, (Lee et al., 2008) low defect density, chemical inertness, (Prasai et al., 2012) and high thermal and electrical conductivity. (Lau et al., 2012; Novoselov et al., 2005) In addition, it is one atomic layer thin and has a bending rigidity comparable to those of biological membranes ($\sim$1 eV) (Nicklow et al., 1972; Fasolino et al., 2007) making it a prototypical membrane material. The low bending rigidity allows graphene to be extremely flexible and conform well to the underlying substrates as evidenced in experiments like Lui et al., (2009) Some studies have realized that graphene's electronic properties can be altered in an useful manner using mechanical strain. (Guinea et al., 2008; Pereira and Castro Neto, 2009; Guinea et al., 2009; Levy et al., 2010) Understanding what makes a graphene membrane conform well or otherwise will help in designing novel electronic devices that will take advantage of the strains that develop as a result of adhesion. In addition, this can aid the design of substrate morphologies to alter the adhesive properties of graphene and other materials which in turn could aid in developing better graphene based protective coatings, transparent electrodes, flexible electronics and nano-electro-mechanical systems. (Prasai et al., 2012; Lanza et al., 2013; Wassei and Kaner, 2010; Yuk et al., 2012; Yan et al., 2012)

In the literature, the effect of substrate morphology on membrane (especially biological/soft membranes) adhesion has been extensively studied in the continuum setting. (Lipowsky and Seifert, 1991; Palasantzas and Backx, 1996; Swain and Andelman, 1999; Pierre-Louis, 2008) The general strategy is to construct a free energy functional, F which includes the elastic bending and stretching strain energies of the membrane (F_{ben} and F_{str}) along with the adhesion energy due to the membrane's interactions with

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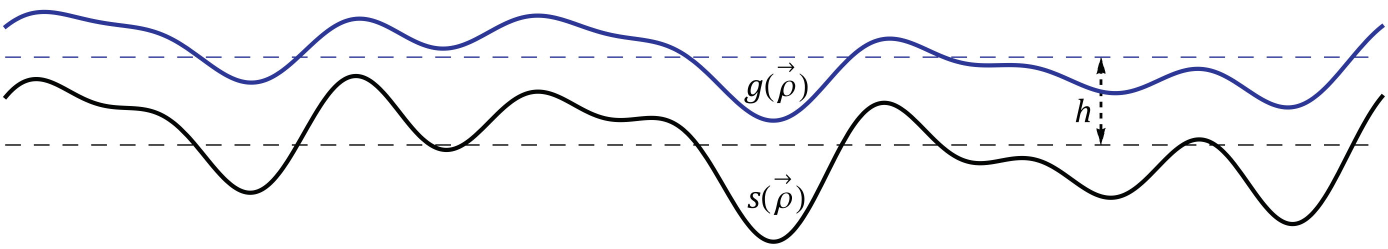

Fig. 1. Illustration showing the morphology of a graphene membrane (blue) on a corrugated substrate (black) with the dashed lines depicting the mean height. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the substrate (F_{adh}). If the substrate topography is described by a function $s(x, y)$, then mathematically the goal is to obtain the shape attained by the membrane, $m(x, y)$ so as to minimize the free energy functional, F.

$$F(m(x,y)) = F_{ben} + F_{str} + F_{adh}, \tag{1}$$

$$\begin{aligned} F_{ben} &= \int dA\ \frac{1}{2}D\Big((\kappa_x+\kappa_y)^2 - 2(1-\nu)\big(\kappa_x\kappa_y - \kappa_{xy}^2\big)\Big) \\ F_{str} &= \int dA\ \frac{1}{2}C\Big((\epsilon_x+\epsilon_y)^2 - 2(1-\nu)\big(\epsilon_x\epsilon_y - \epsilon_{xy}^2\big)\Big) \\ F_{adh} &= \int dA_m \int dV_s V_{pot}(s, m). \end{aligned} \tag{2}$$

Here, dA and dA_m are the area elements on undeformed and deformed membrane respectively, dV_s is the volume element on of the substrate, D and C are bending and stretching rigidities respectively, κ_α and ϵ_α are the membrane curvature and strain along α ($\alpha = x, y$ or xy) and V_{pot} is the interaction potential between the atoms of the substrate and the membrane. With any realistic potential function, this is a complicated problem to solve even numerically. Hence the problem is usually reduced, with companion simplifications, to one dimension with a periodic pattern for the substrate like a sine function.

With the advent of 2D crystals like graphene and the ability to examine their morphology accurately using scanning probe techniques like AFM, this problem has been revisited recently in the literature (Aitken and Huang, 2010; Zhang et al., 2010; Gao et al., 2011; Viola Kusminskiy et al., 2011) with essentially the same continuum approach as described. Each work made the necessary simplifications to arrive at their primary conclusion that the conformity of graphene on a given substrate depends on the substrate morphology, adhesion strength and the number of layers. It has been found that on 1D sinusoidally corrugated substrates, there is a snap through phenomenon where a graphene membrane goes from being non-conformal to conformal as the amplitude or wavelength of the corrugation is changed. Here in this case, conformal is the configuration where the ratio of corrugation amplitudes of graphene membrane and the substrate is close to 1; while non-conformal is the configuration where it is close to zero. This phenomenon has also been observed experimentally. (Scharfenberg et al., 2012) Here in this paper, we pursued this problem to obtain a general understanding of effect of nanoscale roughness on adhesion, both analytically as well as numerically. The analytical approach we take here differs from the existing ones in literature in how the adhesion energy is calculated and we compared our results with those in the literature. Specifically, we use an extended form of Derjaguin approximation to calculate the adhesion energy. The numerical approach departs from the continuum setup altogether by using 'molecular mechanics/statics' simulations. This also allowed us to look at the atomistic details of the adhesion mechanisms of the graphene membranes while validating the continuum model.

We also studied the mechanics of peeling on textured substrates by simulating 'peel test' of a graphene ribbon. Here, we quasi-statically delaminated a graphene nanoribbon by displacing one end perpendicularly to the horizontal plane while pinning the other end. In molecular statics simulations, we observed equilibrium configurations consistent with the ribbons sliding on the substrate. As they slid, the conformity of the ribbon reduces gradually until there is a peel event. After this event, conformity is recovered partially and the ribbon starts to slide again. We noticed that each of the peel events trigger a discontinuity in the magnitude of the peel force and that the peel force has periodicity commensurate with that of the substrates. We developed an approximate theory that captures the essential features of the simulations qualitatively, and reasonably well quantitatively. These results suggest that graphene ribbons might be useful to scan and probe the atomic scale roughness of rigid substrates with the help of the understanding we developed here.

2. Morphology of graphene on textured substrates

2.1. Theory

To reiterate the problem at hand, we considered a graphene membrane adhered to a rigid substrate as illustrated in Fig. 1. Given the functional form of the substrate surface $s(\vec{\rho})$, the goal is to find the functional form of the graphene membrane $g(\vec{\rho})$ ($\vec{\rho}$ being the position vector) with a given operant interaction potential, V_{pot} between the substrate and graphene at the interface. This potential is assumed to be van der Waals interactions (vdW) between atoms that can be described by a Lennard-Jones (LJ) potential. Starting with LJ 6–12 potential $V_{pot}(r) = 4\epsilon((\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6})$ (ϵ is depth of the potential well and σ is the distance at which magnitude of the potential is zero), one can then arrive at a continuum expression via direct integration for the potential, V_f that acts between two flat atomic surfaces separated by a distance h (the subscript f is to signify that this is the potential for two flat surfaces):

$$\begin{aligned} V_f(h) &= \rho_A^2 \int_0^\infty 4\epsilon\left(\left(\frac{\sigma}{(r^2+h^2)^{\frac{1}{2}}}\right)^{12} - \left(\frac{\sigma}{(r^2+h^2)^{\frac{1}{2}}}\right)^{6}\right)2\pi r dr \\ &= -\gamma_0\left(\frac{5}{3}\left(\frac{h_0}{h}\right)^4 - \frac{2}{3}\left(\frac{h_0}{h}\right)^{10}\right). \end{aligned} \tag{3}$$

Here, the integration is done in cylindrical coordinates with the radial coordinate being denoted by r and ρ_A is the areal density of the atoms. It can be easily verified that here $h_0 = \sigma$ is the equilibrium separation where the potential has a minimum and the force between the two flat surfaces is zero. The adhesion energy per unit area, γ_0 is related to other terms via $\gamma_0 = 6\pi\rho_A^2\sigma^2\epsilon/5$. We assumed here that the substrate is just a single layer of atoms without any bulk and has the same density as graphene membrane. We did this to be consistent with the simulations that are

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