ROLE OF INTERFACES ON THE SHEAR STRENGTH AND BENDING PROPERTIES OF VAN DER WAALS TWO-DIMENSIONAL MATERIALS

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EXECUTIVE SUMMARY

Two-dimensional van der Waals materials such as graphene and hexagonal boron nitride (h-BN) are of significant technological importance owing to their unconventional properties at the nanoscale. Using Blue Waters' computational resources, density functional theory calculations and molecular statics simulations were used to quantify the interfacial strength properties of graphene–titanium (Ti) and graphene–aluminum (Al) nanocomposites, as well as the bending rigidity of layered graphene and hexagonal boron nitride nanostructures. The results show that the strongly chemisorbed graphene–Ti interface is drastically weakened by the formation of a metal oxide phase, while the weakly physisorbed graphene–Al interface is significantly strengthened through metal oxide formation. The research team's simulations for the bending rigidity of two- to six-layered boron nitride nanosheets show substantially higher bending stiffness than that of multilayered graphene. These computational results are in excellent agreement with recent experiments.

RESEARCH CHALLENGE

Single-atom sheet nanostructures such as graphene and hexagonal boron nitride offer interesting design capabilities owing to their strong in-plane covalent bonding, with highly tunable but weak van der Waals interactions at the interfaces. For example, graphene or its rolled counterpart, carbon nanotube, can be used as reinforcements in lightweight metal matrix composites (*e.g.*, Ti and Al), leading to high stiffness and strength as well as stability

at high temperatures. This makes them ideal candidates for manufacturing lightweight damage-tolerant structures relevant for the aerospace and automobile industries. Such a unique combination of properties relies on effective bonding along the graphene–metal interface. The local binding properties of graphene on surface-oxidized metals can differ profoundly from those on bare metals, and the associated mechanisms can affect the overall strength of the nanocomposite. On the other hand, the bending rigidity of monolayer 2D materials is simply governed by the underlying chemical bond stretching/compression/rotation behaviors of atoms within the single atomic sheet. However, for multilayer 2D materials, the bending rigidity becomes more complicated owing to the added contributions of interlayer interactions. While monolayer h-BN and graphene have bending rigidities of a similar order of magnitude, the stronger interlayer interaction at h-BN interfaces suggests a potentially different modulus for their multilayer counterparts. Simulations of such local behavior with atomistic details can uncover key mechanisms that are otherwise inaccessible through state-of-the art experiments.

METHODS & CODES

The research team performed density functional theory (DFT) calculations for graphene–metal interfaces using the Vienna Ab initio Simulation Package. They used Projector Augmented Wave-based pseudopotentials to represent the interaction between ionic cores and valence electrons, while the local density approximation was adopted for exchange and correlation. Electronic energy of the structures was minimized by the conjugate gradient method. The team determined the binding properties at the interfaces of graphene–metals, with and without oxidation, by computing electron localization functions that describe the probability of finding one electron in the neighborhood of another electron. Interfacial shear strength was extracted by computing the sliding potential energy surface as a function of relative interfacial displacements.

To investigate the bending and interlayer shear rigidities of h-BN and graphene nanosheets, the research team conducted molecular static simulations using the classical molecular dynamics code LAMMPS. The team adopted a recently developed Tersoff parametrization to represent the intralayer interactions in h-BN. The intralayer atomistic interactions between C atoms in graphene were governed by a second-generation reactive em-

pirical bond order potential. The interlayer interactions for both graphene and h-BN were described by registry-dependent Kolmogorov–Crespi-type force fields. The group performed stiffness calculations of folded h-BN and graphene sheets with varying numbers of interlayers by first constructing sinusoidally modulated initial geometries and minimizing their energies by the conjugate gradient method.

RESULTS & IMPACT

In Fig. 1, the DFT simulations suggest opposite changes to the binding and shear strength properties of graphene on these two types of metals when surface oxidized [1]. The researchers observed distinctly higher electron localization function values of approximately 0.3 across Ti–graphene versus approximately 0.1 across Al–graphene because of hybridization of the unoccupied d-orbitals in transition Ti metal with the $2p$-orbitals of C atoms in graphene. For graphene on Ti–O and Al–O substrates, the Ti–C and Al–C interactions are weakened by O atoms on the metal surface. The high interfacial shear strength of approximately 5 GPa along pure Ti/graphene is reduced by two orders of magnitude to approximately 20 MPa along Ti–O/graphene, while the interfacial shear strength of approximately 10 MPa along pure Al/graphene remains similar in magnitude along Al–O/graphene. These fundamental insights on graphene–metal interfaces have important implications for graphene-reinforced metal matrix composites and the fabrication of graphene–metal contacts in graphene transistors, as well as the transfer printing and epitaxial growth of graphene on metallic substrates.

The research group's simulations showed that the bending properties of multilayer h-BN and graphene are significantly different from their monolayer counterparts [2]. While the bending stiffness of monolayer h-BN and graphene is associated with pure bending of the single atomic layer, the stiffness of folded two- to six-layered h-BN and graphene has added contributions from interlayer sliding and out-of-plane deformation. Figs. 2b and 2c show the relative change in the normal (δ_n) and shear (δ_s) separations of the three interlayers (L_1-L_3) for the folded four-layer h-BN and graphene sheets depicted in Fig. 2a. The interlayer deformation localizes near the steepest slope of the folded configurations, as marked by red dashed lines in Fig. 2a, and results in significant distortions in stacking sequences for h-BN and graphene (insets of Fig. 2a). For h-BN, the relatively stronger binding between interlayers and the higher barrier energies for interlayer sliding result in smaller normal (Fig. 2b) and shear separations (Fig. 2c) compared to graphene. This explains the consistently higher effective stiffness of folded multilayer h-BN versus observations in recent experiments.

WHY BLUE WATERS

Blue Waters' resources were required for the evaluation of multiple graphene–metal/metal oxide nanostructures (approximately 20 different structures) with several hundred atoms per structure in DFT. Bending stiffness computations of folded h-BN and
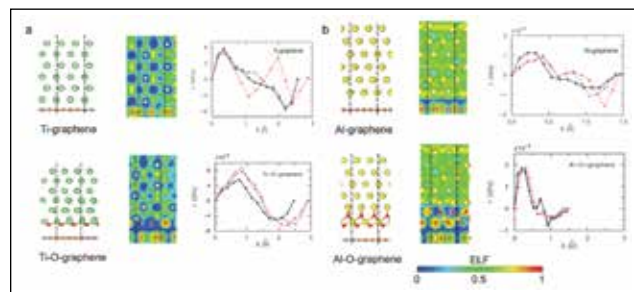

Figure 1: Effect of oxidation on the interfacial binding and shearing properties in titanium–graphene (a) and aluminum–graphene (b) interfaces. The figures in the upper and lower panels of (a) and (b) show (from left to right) the atomic structure, electron localization function contours, and shear stress response with relative sliding of the interfaces.
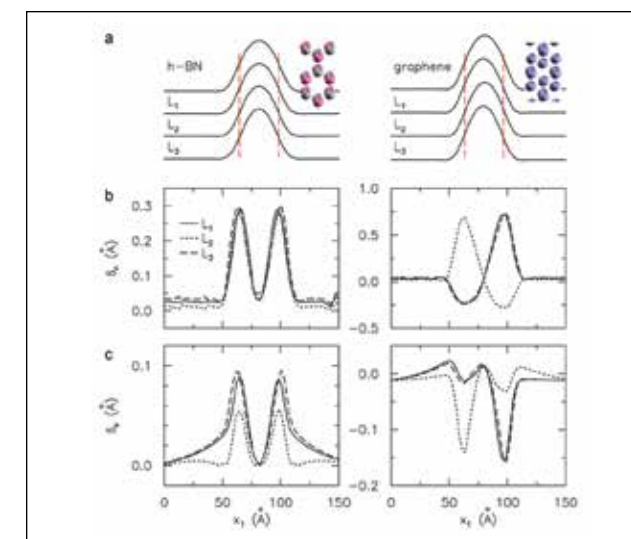

Figure 2: Folded geometries (a), with interlayer normal (b) and shear (c) separations in four-layer h-BN (left) and graphene (right) nanostructures. Stacking deviations, as viewed from the top, in inset (a) at locations of maximum normal and shear separations indicated by red dashed lines; pink, grey, and blue denote boron, nitrogen, and carbon atoms, respectively.

graphene nanostructures (comprised of hundreds of thousands of atoms per structure) using classical molecular dynamics simulations based on many-body potentials necessitated the massively parallel computing capabilities of Blue Waters.

PUBLICATIONS & DATA SETS

C. Yi *et al.*, "Direct nanomechanical characterization of carbon nanotubes-titanium interfaces," *Carbon*, vol. 132, pp. 548–555, 2018.

S. Bagchi, A. Harpale, and H. B. Chew, "Interfacial load transfer mechanisms in carbon nanotube-polymer nanocomposites," *Proc. Royal Soc. Lond. A*, vol. 474, Art. no. 20170705, 2018.

C. Yi, S. Bagchi, F. Gou, C.M. Dmuchowski, C. Park, C. C. Fay, H. B. Chew, and C. Ke, "Direct nanomechanical measurements of boron nitride nanotube–ceramic interfaces," *Nanotechnol.*, vol. 30, Art. no. 025706, 2018.

S. Bagchi, C. Ke, and H. B. Chew, "Oxidation effect on the shear strength of graphene on aluminum and titanium surfaces," *Phys. Rev. B*, vol. 98, Art. no. 174106, 2018.

S. S. Sawant, P. Rao, A. Harpale, H. B. Chew, and D. A. Levin, "Multi-scale thermal response modeling of an AVCOAT-like thermal protection material," *Int. J. Heat Mass Transf.*, vol. 133, pp. 1176–1195, 2019.

Y. Cui, and H. B. Chew, "A simple numerical approach for reconstructing the atomic stresses at grain boundaries from quantum-mechanical calculations," *J. Chem. Phys.*, vol. 150, Art. no. 144702, 2019.

W. Qu, S. Bagchi, X. Chen, H. B. Chew, and C. Ke, "Bending and interlayer shear moduli of ultrathin boron nitride nanosheet," *J. Phys. D: Appl. Phys.*, vol. 52, no. 46, pp. 465301, 2019.