

Molecular dynamics prediction of interfacial strength and validation through atomic force microscopy

Ulises Galan and Henry A. Sodano

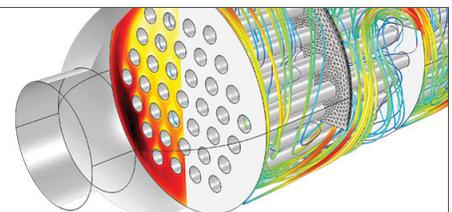
Citation: [Applied Physics Letters](#) **101**, 151603 (2012); doi: 10.1063/1.4758988

View online: <http://dx.doi.org/10.1063/1.4758988>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/101/15?ver=pdfcov>

Published by the [AIP Publishing](#)

Over **700** papers & presentations on multiphysics simulation



VIEW NOW ►

 COMSOL

Molecular dynamics prediction of interfacial strength and validation through atomic force microscopy

Ulises Galan¹ and Henry A. Sodano^{2,3}

¹School for Engineering of Matter, Transport and Energy, Arizona State University, Arizona 85287, USA

²Department of Mechanical and Aerospace Engineering, University of Florida, Florida 32611, USA

³Department of Materials Science and Engineering, University of Florida, Florida 32611, USA

(Received 12 July 2012; accepted 28 September 2012; published online 11 October 2012)

Molecular dynamics (MD) simulations are performed to calculate the interfacial energy between zinc oxide (ZnO) and graphitic carbon. The MD model consists of a ZnO slab and a single layer of graphitic carbon. The calculation was validated experimentally by atomic force microscopy (AFM) liftoff. A polishing process was applied to create a tip with a flat surface that was subsequently coated with a ZnO film allowing force displacement measurement on highly oriented pyrolytic graphite to validate the simulations. The MD simulation and AFM lift-off show good agreement with adhesive energies of 0.303 J/m^2 and $0.261 \pm 0.054 \text{ J/m}^2$, respectively. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4758988>]

The mechanics of adhesion between two solids is an important physical process with implications in many technological fields. When two distinct solid surfaces approach, atomic forces and surface energies define the macroscopic properties of the interface. Many approaches exist to model this phenomenon, such as electronic-structure calculations which have been used to characterize the interface between magnesium oxide (MgO) and silver (Ag),¹ silicon carbide (SiC) (001) and aluminum (Al),² α -aluminum oxide (Al₂O₃) (0001) and copper (Cu) (111)³ among others. Molecular dynamics (MD) simulations have also been employed to investigate the mechanical properties of materials and interfaces at the atomic scale with models larger than those easily simulated with *ab initio*, for example the interface energy between Al and SiC.⁴ These types of studies have been useful to gain better understanding of the mechanics of separation between two solids. However, the simulation results are not often validated due to challenges replicating the simulated surfaces experimentally and the typically defect-free nature of the simulations. Here, we will seek to employ atomic force microscopy (AFM), which has been widely used to measure forces caused by atomic interactions between the tip and a substrate to validate the simulations. AFM makes indirect measurement of the forces and depends on the surface of the tip,⁵ for example functionalized tips have been used to identify the mechanism of adhesion between substrates and molecules.^{6,7}

Recently Lin *et al.*⁸ employed zinc oxide (ZnO) nanowires (NWs) as an interphase between the carbon fibers and polymer matrix in fiber reinforced composites and demonstrated a more than two times increase in the interfacial shear strength compared to bare fibers. The research was extended to investigate the properties of ZnO NWs on aramid fibers⁹ as well as to study the role of morphology in the interfacial,¹⁰ ultimately achieving 3.27 times the interface strength offered by a composites grade epoxy. The results suggested that the adhesion of the ZnO NWs with the fibers was responsible for the improved interfacial shear strength. In this context, the study of the surface interactions between ZnO and carbon offers the potential for further enhancement to

this system as well as the general problem of adhesion to graphitic surfaces. With the aim to better understand the mechanical properties between ZnO and carbon, we develop a MD model and validate the model with AFM lift off measurements from the surface of highly oriented pyrolytic graphite (HOPG) using a ZnO coated AFM tip.

MD simulates the atomic interactions that govern the energetics and properties of a material by describing these interactions with a force field and assuming atoms as single points with a defined mass.¹¹ A range of material properties such as adhesion, diffusion, cracking, and creep can be studied by applying the laws of classical mechanics, thus MD provides a tool to study systems at an atomic level. The attractive and repulsive forces that arise at the atomic scale are defined by a force field can be divided into bonded and non-bonded interactions for neutral systems, while ionic interactions are accounted for by the summation of the electrostatic energies. The ionic interactions in ZnO can be described by pairwise interactions with the Buckingham¹² force field and the charges of the ions can be described through the Ewald method.¹³ In the case of graphitic carbon, the optimized potential for liquid simulations (OPLS)¹⁴ is used, which includes bonded, non-bonded, angular, and torsional parameters. The Zn-Carbon and O-Carbon parameters were taken from Refs. 15 and 16, respectively, and apply to the Lennard-Jones potential which is used to describe nonbonded interactions. For the MD model, the large-scale atomic molecular massively parallel simulator (LAMMPS)¹⁷ has been used to perform the simulation. The MD model of the interface consists of ZnO slab with free surfaces and a single layer of graphite (graphene) at the bottom of the ZnO slab.

ZnO is an ionic solid with wurtzite structure and lattice parameters of $a = 3.25$ and $c = 5.20$. The structure consists of alternating planes of coordinated O²⁻ and Zn²⁺ ions along the c axis producing a dipole moment along this axis that gives rise to polar surfaces. The polar surfaces are Tasker type III (Ref. 18) either Zn (0001) or O (000 $\bar{1}$) terminated and the structure generates an electrostatic field perpendicular to the surfaces; the accumulation of electrostatic energy causes the surface energy to diverge and instability of the

structure. These surfaces have been discussed in the literature^{18–21} and it has been found that the surface morphologies are dependent on the polarity of the surfaces. One way to stabilize the structure is by removing one fourth of Zn atoms from the (0001) surface.²² Still further research has shown that the (0001) surface undertakes triangular shape reconstruction in the stabilization process.¹⁹ For the MD model used here, ZnO was constructed with periodic boundary conditions in the X and Y directions to give stability to the relaxed structure. The Z direction is not periodic and was stabilized considering two cases of the polar surfaces. First, one fourth of Zn atoms was removed from the Zn terminated surface; while in the second case, triangular voids were formed at the (0001) surface.¹⁹ The edges of the holes have oxygen atoms and the dimension of the edge was 9.3 Å. In both cases, a stable configuration was achieved. The dimensions of the structure were 42 Å by 38 Å by 20 Å. In the first case with one fourth of the Zn atoms removed, the ZnO model has a total of 2912 atoms and in the second case with triangular voids a total of 2765 atoms. ZnO has multiple nonpolar surfaces, and in these surfaces, the energy is finite and it is possible to have stable free surfaces without distortion of the ideal wurtzite crystal structure. With the aim to capture the main properties of the ZnO crystals deposited on the AFM tip here, we also performed a simulation on the (1100) nonpolar surface, with the model having 2912 atoms and only relaxation of the structure being necessary.

In order to achieve a stable configuration of graphene, the edges were terminated by hydrogen atoms; this condition also allows graphene to achieve zero residual stress in the lateral directions independent of the size of LAMMPS simulation box. The dimension of the graphene layer was 32 Å by 28 Å, slightly smaller than that of the ZnO. Since the simulation box is adjusted to the size of ZnO, both ZnO and graphene have zero residual stress in the lateral direction independent of the mismatch in the dimensions of each structure. The residual stress may also be eliminated without hydrogen atoms on the edge of graphene by increasing the size of the structures until the dimensional mismatch becomes insignificant. However, this technique increases the computational cost without improving the accuracy of the simulation and it was not considered here.

In order to validate the accuracy of the potentials, the first step is to calculate the properties of each structure in the stable, isolated form. Bulk ZnO was simulated resulting in a lattice energy of -39.34 eV and density of 5.65 g/cm³. Graphene was simulated and upon relaxation, the lattice cohesive energy was 8.65 eV/atom in agreement with known values. The ZnO and graphene structures were then combined into a single model with a total of 3270 atoms and relaxed together in order to achieve zero global stress. The isothermal-isobaric ensemble²³ (NPT) was used to obtain zero stress at the X and Y boundaries of ZnO. Specifically, the temperature was set to 100 K and the system was simulated for 20 ps with the temperature gradually reduced to 1 K in the interval of 20 ps while keeping the NPT ensemble. The canonical ensemble (NVT)^{24,25} was used to keep the volume constant and temperature of about 1 K for 20 ps.

After relaxation, the NVT ensemble was used to keep the temperature constant, and a displacement was applied to

the graphene to simulate liftoff. The positions of the atoms at the top of ZnO were fixed in space, these atoms are shown in the shaded area of Figure 2; graphene was separated in the negative Z direction while the rest of the atoms of ZnO was allowed to deform through the interaction forces with the graphene layer. During the simulation, the stress on the graphene was recorded. The layer of graphene was displaced by steps of 0.25 Å and the structure was allowed to equilibrate for 20 ps in between each step, to yield a test velocity of 1.25 m/s. The stress on graphene during the liftoff is shown in Figure 1. The first step of separation generated an adhesive force of 9.8 nN which rose rapidly in the subsequent steps to achieve a maximum adhesive force of 14.7 nN at 0.75 Å of separation. The force then begins a more gradual decline and is approximately zero nN at 7 Å. For the polar surface, both ZnO stabilization cases, one fourth of Zn atoms removal and triangular void stabilization were considered in the simulated separation and the results obtained were the same. For the (1100) nonpolar surface, the separation simulation was performed with nearly the same results as the polar surface. The interface energy was calculated by integrating the force displacement curve to yield a total liftoff energy of 2.734 aJ. Normalizing by the area of the graphene surface (896 Å²) gives a specific liftoff energy of 0.303 J/m².

The extreme sensitivity of an AFM makes it possible to measure forces based on the atomic interaction between two materials, which defines the adhesive properties of the interface.⁶ In order to have an accurate force measurement, it is necessary to know the spring constant of the AFM cantilever to relate displacements to atomic forces between the tip and substrate. The experiment employed here uses a cantilever AFM probe calibrated according to the method by Sader,²⁶ and the cantilever (MikroMasch, San Jose, CA, USA) had a spring constant of 0.122 N/m \pm 10% and used on a Park AFM XE-70. AFM tips are typically designed to be atomically sharp; however this experiment requires a flat tip with known surface area to quantify the energy of adhesion per surface area such that comparisons with the MD model can be made. The silicon tip was flattened via a polishing over a diamond lapping film with a grain size of 0.1 μm to create a smooth surface and one that accounts for the slope in the

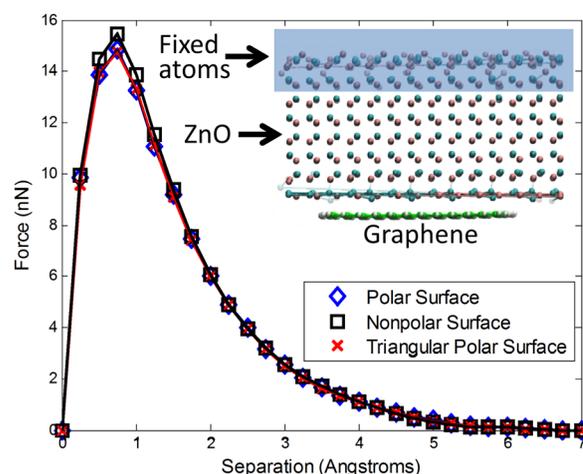


FIG. 1. Force displacement curve on carbon atoms for the separation between the two materials as calculated with LAMMPS.

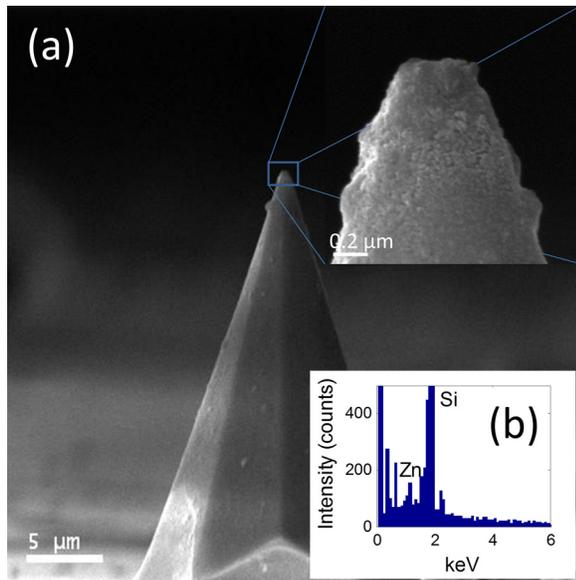


FIG. 2. (a) Flat surface of AFM tip after polishing and (b) EDX showing Zn.

cantilever such that the flattened tip is parallel to the substrate surface. Once polished, the surface area of the tip was measured in a scanning electron microscope to be $0.067 \mu\text{m}^2$, as shown in Figure 2. The uncoated polished tip was repeatedly tested with HOPG and the interface energy was measured to be 0.087 J/m^2 with a standard deviation of 0.0071 J/m^2 , as shown in Figure 3 (blue squares).

The thin, conformal ZnO film was created through the deposition and coalescence of ZnO nanoparticles. The ZnO nanoparticles were synthesized following the methods of Hu *et al.*²⁷ to obtain a stable colloidal suspension of nanoparticles. Once the solution was ready, the AFM tip was dipped into the solution and then put into an oven at 70°C for 3 min. This process was repeated seven times to form a thin layer of

ZnO on the tip. Energy dispersive x-ray spectroscopy in a scanning electron microscope confirmed the formation of the ZnO layer on the surface of the AFM tip and is shown in the inset of Figure 2.

Once the tip was coated with ZnO, force displacement measurements were taken under the AFM with a fresh HOPG surface. The AFM tip approaches the surface of HOPG and a small force is applied that deflects the cantilever to a load of 40 nN. The cantilever then retracts, but because of the adhesion between the surfaces, the tip does not separate from the substrate. Eventually, the force reaches a limit where the tip separates from the substrate allowing the adhesion energy as shown by the shaded area of the force displacement curve²⁸ in Figure 3(b) to be measured.

The presence of ZnO on the AFM tip produces a higher energy of adhesion as shown in Figure 3. As a calibration of the testing procedure, the ZnO layer was then removed using an acid solution (HCl) and the testing was repeated, producing the same adhesive energy prior to coating with ZnO. This both demonstrated the repeatability of the test as well as the validity of the approach. A layer of gold was sputter coated on top to serve as a reflective surface that is unaffected by the acid cleaning. The tip was then recoated with ZnO using the same process and the interface energy was measured followed by cleaning of the tip in acid and testing on a cleared HOPG surface. The measurements were confirmed by repeating this process three additional times, with the mean for each set of tests shown in Figure 3. The average value for the energy of adhesion was 0.261 J/m^2 with a standard deviation of 0.054 J/m^2 for the ZnO HOPG interface.

The liftoff testing demonstrates the strong adhesive energy between ZnO and HOPG. Furthermore, the results from the simulation and the AFM liftoff test show good agreement. It should, however, be noted that the nature of the experiment is somewhat different from the simulation. Specifically, in the AFM liftoff, the cantilever deflects and the two surfaces separate because of the potential energy accumulated in the cantilever beam. In the case of MD, the separation was applied along the Z direction, graphene was assumed to move rigidly, and the reaction forces are recorded by LAMMPS and integrated to measure the adhesive energy. The calculation of the energy of adhesion between ZnO and HOPG was computed through the force displacement curves of a liftoff experiment. In both the MD simulation and the AFM liftoff experiment, the adhesive energy is similar, with the MD model yielding 0.303 J/m^2 and the AFM experiments yielding $0.261 \pm 0.054 \text{ J/m}^2$. The nature of the AFM liftoff experiment measures the adhesion energy by computing the area formed by the shaded triangle as shown in Figure 3. The force measured at the moment of separation in the AFM was $66.53 \pm 7.46 \text{ nN}$. The MD simulation recorded a maximum force of 14.7 nN. This difference stems from the nature of the experimental setups because the AFM cantilever beam stores all of the potential energy needed to separate the surfaces before the interface fails with an abrupt change in force. The MD simulation of the interface computes the force as the graphene and the ZnO separate, a process that is not possible to do experimentally. This can be seen in Figure 1, the force reaches the maximum and decays slowly because the interaction forces and more

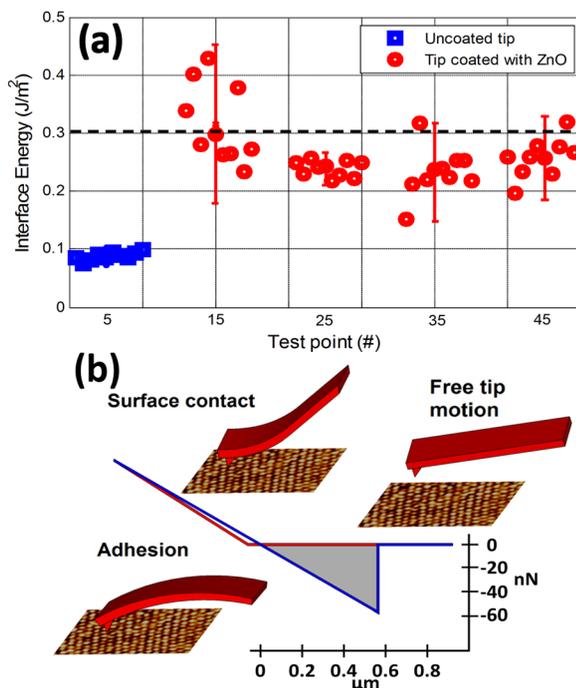


FIG. 3. (a) Results of AFM test. Blue square uncoated tip, red point tip coated with ZnO. (b) Typical force displacement curve.

generally the force field used to represent the interaction of each atomic species across the interface, whereas in AFM measurement and the force displacement curve shows a triangular area that decays sharply once the tips separates from HOPG. Since the shape of the force displacement curves is different, the same maximum force is not expected. However in both cases, the force-displacement curve is used to calculate the adhesive energy per surface area.

To understand the difference in adhesive energy between Si-HOPG and ZnO-HOPG is important to look at the properties of ZnO and Si. The primary difference is that ZnO has ionic bonding caused by electrostatic forces whereas Si is covalently bonded. In the ZnO crystal, the addition of electrostatic energy in the *c* axis causes the energy to diverge at the polar surface,¹⁸ thus a stabilization mechanism takes place. Here two mechanism of stabilization were simulated and the results showed the same adhesion energy 0.303 J/m^2 when graphene was separated from ZnO polar surface. Also the nonpolar surface (1100) was considered, in this case the ideal crystal structure was not modified because of its own stability, and the adhesion energy was measured to also be 0.303 J/m^2 . The result suggests that the absorption properties of ZnO surfaces will not affect the adhesion to graphene because graphene's surface is inert. On the other hand, Si is a covalently bonded material, with symmetric configuration on the surfaces, for example Si (100)- 2×1 and Si (111)- 7×7 .²⁹ The results of the AFM test suggest that the higher adhesive energy between ZnO and HOPG is caused by electrostatic forces. This type of force is known to increase adhesion and in some cases the attractive forces can be as large as cohesive forces in covalent-ionic solids.³⁰ In the case of Si, the adhesion energy will come only from Van der Waals forces since Si and HOPG are two covalently bonded materials. The measurements performed with the AFM are in agreement with known values of Van der Waals adhesive energy, which is typically $<0.11 \text{ J/m}^2$.

This letter has investigated the adhesion between ZnO and graphite, which was recently shown to provide 3.28 times higher shear strength than epoxy in fiber reinforced composites.¹⁰ The adhesion was simulated using MD and shown to have an adhesive energy of 0.303 J/m^2 which is more than 4.3 times higher than predicted between carbon nanotubes and epoxy.³¹ The strong bonding present between ZnO and carbon may lead to methods for the enhancement of organic interfaces through the use of inorganic interphase.

Additionally, the simulations were validated through AFM lift off studies that showed very good agreement with the models. This validation approach can be used to further enhance the impact of numerical predictions of properties in solid-solid interfaces.

The authors would like to acknowledge the Army Research Office (Award # W911NF0810382) and Dr. David Stepp for funding of this project.

- ¹J. A. Purton, D. M. Bird, S. C. Parker, and D. W. Bullett, *J. Chem. Phys.* **110**, 8090 (1999).
- ²J. Hoekstra and M. Kohyama, *Phys. Rev. B* **57**, 2334 (1998).
- ³S. Tanaka, R. Yang, and M. Kohyama, *Philos. Mag.* **86**, 5123 (2006).
- ⁴C. R. Dandekar, *Composites, Part A* **42**, 355 (2011).
- ⁵T. Eastman and D.-M. Zhu, *Langmuir* **12**, 2859 (1996).
- ⁶E. L. Florin, V. T. Moy, and H. E. Gaub, *Science* **264**, 415 (1994).
- ⁷T. Han, J. M. Williams, and T. P. Beebe Jr., *Anal. Chim. Acta* **307**, 365 (1995).
- ⁸Y. Lin, G. Ehlert, and H. A. Sodano, *Adv. Funct. Mater.* **19**, 2654 (2009).
- ⁹G. J. Ehlert and H. A. Sodano, *ACS Appl. Mater. Interfaces* **1**, 1827 (2009).
- ¹⁰U. Galan, *Compos. Sci. Technol.* **71**, 946 (2011).
- ¹¹J.-P. Ryckaert, G. Ciccotti, and H. J. C. Berendsen, *J. Comput. Phys.* **23**, 327 (1977).
- ¹²D. J. Binks, D. York, and L. Pedersen, Ph.D. dissertation, University of Surrey, Harwell, 1994.
- ¹³T. Darden, D. York, and L. Pedersen, *J. Chem. Phys.* **98**, 10089 (1993).
- ¹⁴W. L. Jorgensen, D. S. Maxwell, and J. Tirado-Rives, *J. Am. Chem. Soc.* **118**, 11225 (1996).
- ¹⁵J. Y. Guo, C. X. Xu, B. X. Gu, and F. Y. Sheng, *J. Appl. Phys.* **109**, 024307 (2011).
- ¹⁶J. G. Harris, *J. Phys. Chem.* **99**, 12021 (1995).
- ¹⁷S. Plimpton, *J. Comput. Phys.* **117**, 1 (1995).
- ¹⁸P. W. Tasker, *J. Phys. C* **12**, 4977 (1979).
- ¹⁹O. Dulub, U. Diebold, and G. Kresse, *Phys. Rev. Lett.* **90**, 16102 (2003).
- ²⁰G. Kresse, O. Dulub, and U. Diebold, *Phys. Rev. B* **68**, 245409 (2003).
- ²¹Y.-M. Yu and B.-G. Liu, *Phys. Rev. B* **77**, 195327 (2008).
- ²²G. Heiland and P. Kunstmann, *Surf. Sci.* **13**, 72 (1969).
- ²³H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, A. DiNola, and J. R. Haak, *J. Chem. Phys.* **81**, 3684 (1984).
- ²⁴S. Nosé and M. L. Klein, *Mol. Phys.* **50**, 1055 (1983).
- ²⁵H. C. Andersen, *J. Chem. Phys.* **72**, 2384 (1980).
- ²⁶J. E. Sader, I. Larson, P. Mulvaney, and L. R. White, *Rev. Sci. Instrum.* **66**, 3789 (1995).
- ²⁷Z. Hu, G. Oskam, and P. C. Searson, *J. Colloid Interface Sci.* **263**, 454 (2003).
- ²⁸R. W. Carpick, D. F. Ogletree, and M. Salmeron, *J. Colloid Interface. Sci.* **211**, 395 (1999).
- ²⁹T. R. Leftwich and A. V. Teplyakov, *Surf. Sci. Rep.* **63**, 1 (2008).
- ³⁰R. G. Horn and D. T. Smith, *Science* **256**, 362 (1992).
- ³¹J. Gou, B. Minaie, B. Wang, Z. Liang, and C. Zhang, *Comput. Mater. Sci.* **31**, 225 (2004).