DI

TN

FS

BI

ELECTRON DYNAMICS OF ION-IRRADIATED GRAPHENE

Allocation: Illinois/550 Knh
PI: André Schleife[1]
Co-PI: Alina Kononov[1]

[1]University of Illinois at Urbana-Champaign

EXECUTIVE SUMMARY

Two-dimensional materials like graphene possess a variety of unique properties desirable for diverse applications. However, developing novel technologies and devices often depends on high-resolution techniques for imaging and manipulating these promising materials. Such techniques include focused ion beams, making it critically important to understand the response of 2D materials to ion irradiation. Although the response of bulk materials to ion irradiation has been well-studied, a comprehensive description of the response of thin materials and material surfaces is lacking. We investigated the dependence of charge transfer, energy transfer, and secondary-electron yield on graphene thickness and ion species, charge, velocity, and trajectory when an ion traverses graphene. Our results provide unprecedented insight into these dynamical processes, and inform the improvement of ion-beam techniques for thin materials.

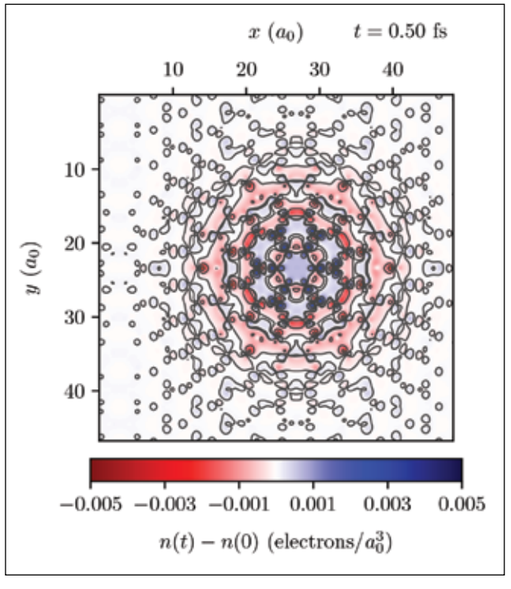

Figure 1: Visualization of local charge in graphene about 0.5 femtoseconds after a proton impacts the material. Blue indicates negative charge while red indicates positive charge.

RESEARCH CHALLENGE

The high conductivity, transparency, mechanical strength, flexibility, and chemical stability of graphene make it a promising candidate for a wide variety of applications, including solar cells, supercapacitors, transparent electrodes, flexible electronics, water desalination, and more [1,2]. However, its properties are extremely sensitive to defects, nanopores, functionalization, and other types of nanostructure, whether intentional or not [3,4]. Thus, developing graphene-based devices requires efficient, reliable, and scalable imaging and patterning techniques for high-resolution characterization and manipulation of its nanostructure.

A variety of materials science imaging and processing techniques involve focused beams of charged particles interacting with materials. Typical microscopy techniques detect secondary electrons emitted by the sample after excitation by energetic particles. On the other hand, typical patterning techniques use ion beams to eject atoms from the sample and/or implant defects, modifying the nanostructure. Since the response of the material depends strongly on the charge, mass, and velocity of the ions used, these parameters must be optimized for the desired application.

Optimizing ion beam parameters for imaging and processing graphene and other two-dimensional materials requires a detailed understanding of the ultrafast electron–ion dynamics occurring during ion irradiation of these materials. As a first-principles study of the electronic response of graphene to irradiation by a variety of ion species across a range of velocities, this project provides unprecedented insight into the ultrafast electron–ion dynamics occurring during the interaction of graphene with various types of ion beams. Our work not only informs ion beam techniques for graphene but also lays the foundation for systematic prediction of the most effective imaging and processing methods for other two-dimensional materials and their heterostructures. This ultimately will accelerate the development of innovative technologies based on these materials, which could revolutionize personal electronics and the energy industry.

METHODS & CODES

We use Qbox/Qb@ll [5], our highly parallel implementation of Ehrenfest molecular dynamics and real-time, time-dependent density functional theory [6], to perform accurate first-principles simulations of excited-electron dynamics. This approach treats nuclei as classical point charges interacting electrostatically with electrons. Electrons are treated quantum-mechanically; their quantum orbitals, represented in a plane-wave basis, are governed by the Kohn–Sham equations. We use the common adiabatic local-density approximation for the exchange-correlation potential that describes the quantum correction to the electron–electron interaction.

The simulations generate a time-dependent electron density, which is further analyzed to extract the secondary electron yield and the charge transferred to the projectile, among other quantities. Fig. 1 shows a visualization of the change in electron density, or the local charge, in the graphene about 0.5 femtoseconds after impact by a 25 keV proton.

Starting with the lowest energy configuration of the material as the initial condition, the electronic orbitals are propagated through time by numerically integrating the time-dependent Kohn–Sham equations. We tested several different integrators, concluding that enforced time-reversal symmetry (ETRS) is the most efficient option, proving to be more stable and much more accurate than the popular fourth-order Runge–Kutta method. We also laid the groundwork for the future exploration of better integrators for our code. We acknowledge support from the National Science Foundation under Grant No. OAC 17–40219.

RESULTS & IMPACT

We examined the dependence of the secondary electron yield, charge transfer, and energy transfer on projectile type, velocity, and trajectory, allowing us to evaluate the suitability of certain parameter combinations for imaging two-dimensional materials. For example, as illustrated in Fig. 2, we found that secondary electron yield remains nearly constant for 25–80 keV protons impacting graphene. Since energy transfer increases with proton energy in this energy range, these findings suggest that proton energies of 25 keV and below are optimal for imaging applications, where high secondary-electron emission coupled with low damage to the material are desirable.

The data we obtained informs the controlled application of ion-beam techniques, which promise higher resolution and versatility than traditional tools for imaging and nanostructuring of graphene and other two-dimensional materials. Our approach enables predicting parameter combinations that are suitable for nondestructive imaging of graphene or for intentionally introducing defects in thin materials. By simultaneously studying charge transfer, secondary electron emission, and their ultrafast dynamics, our work also advances the understanding of the fundamental physics occurring during the interaction of a material with ion irradiation.

WHY BLUE WATERS

Blue Waters enabled us to conduct the long simulations of large systems involved in this project. To accurately model the secondary electron emission from a 2D material under irradiation, we must have the capability to evolve thousands of electrons over thousands of timesteps in an elongated simulation cell containing a large vacuum outside the material. These aspects make the simulations computationally expensive; they are only possible with a massively parallel implementation of the first-principles approach and a high-performance supercomputer. Blue Waters allowed us to compute detailed information about more than 20 setups with different graphene thicknesses and projectile species, charges, velocities, and trajectories.

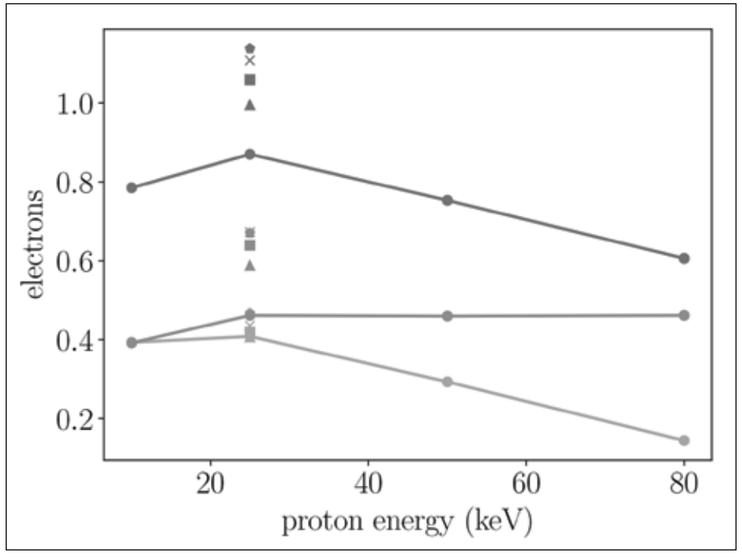

Figure 2: Visualization of local charge in graphene about 0.5 femtoseconds after a proton impacts the material. Blue indicates negative charge while red indicates positive charge.