Supporting Online Material for

Anomalous Strength Characteristics of Tilt Grain Boundaries in Graphene

Rassin Grantab, Vivek B. Shenoy,* Rodney S. Ruoff*

*To whom correspondence should be addressed.
E-mail: vivek_shenoy@brown.edu (V.B.S.); r.ruoff@mail.utexas.edu (R.S.R.)

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Anomalous Strength Characteristics of Tilt Grain Boundaries in Graphene - Supporting Online Material

Rassin Grantab[1], Vivek B. Shenoy[1*], Rodney S. Ruoff[2*]

[1]Division of Engineering, Brown University, Providence, RI, 02906, USA

[2]Department of Mechanical Engineering and The Texas Materials Institute,
The University of Texas, Austin, TX, 78712, USA

1 Computational methods

Molecular Dynamics (MD) simulations were performed using the package, LAMMPS (*1*). All simulations were performed on 80Å square graphene sheets; the tilt grain boundaries were placed in the middle of the sheets and were oriented parallel to the Y-direction. The graphene sheets were deformed under tensile loading in directions perpendicular (along the X-axis) and parallel (along the Y-axis) to the grain boundaries at a constant strain-rate until complete failure was observed. A 2.5Å wide strip of material at each end of the sheet was constrained against motion along the direction of deformation (but free to move in the direction perpendicular to the direction of deformation) by enforcing zero force and velocity on the atoms in these regions. With these constraints in place, the sheets were subsequently relaxed for 10000 MD steps, then a homogeneous strain of 0.5% was applied to the graphene sheets by scaling all atomic coordinates accordingly; using a time step of $1fs$, this results in an average strain-rate of $0.05\%ps^{-1}$. This procedure of relaxation and stretching was applied sequentially until complete failure of each graphene sheet. All MD simulations were performed using an NVE ensemble.

An adaptive intermolecular reactive bond order (AIREBO) potential (*2*) as implemented in LAMMPS, was used to model the atomic interactions in graphene. Following the work of Pei *et*

al. (*3*), we have used an interaction cut-off parameter of 1.92Å. In order to calculate the stress-strain curves during deformation, the stress on each individual carbon atom was first calculated according to the following Virial stress expression (*4, 5*):

$$\sigma_{ij}^{\alpha} = \frac{1}{\Omega^{\alpha}}\left(\frac{1}{2}m^{\alpha}v_i^{\alpha}v_j^{\alpha} + \sum_{\beta=1,n} r_{\alpha\beta}^{j} f_{\alpha\beta}^{i}\right) \tag{1}$$

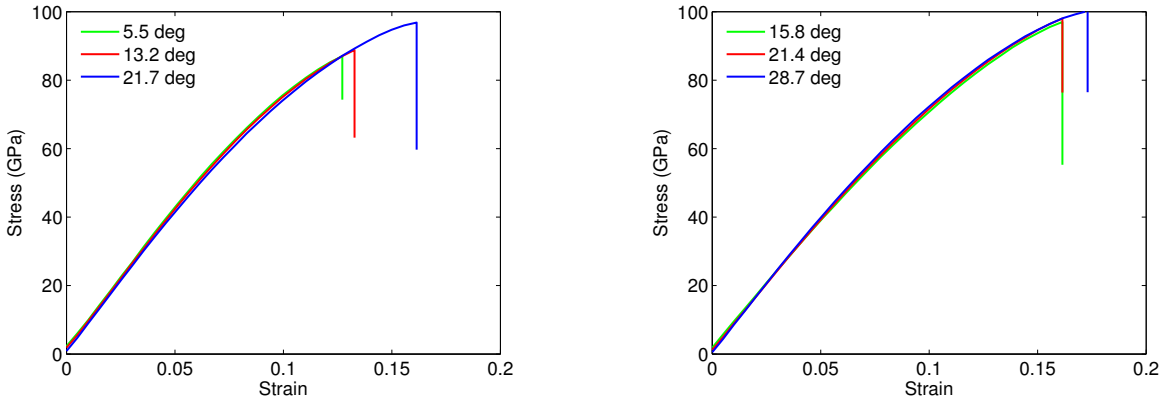
In the equation above, i and j denote the indices in the Cartesian coordinate system, while α and β are the atomic indices; m^{α} and v^{α} are the mass and velocity of atom α, respectively; $r_{\alpha\beta}$ and $f_{\alpha\beta}$ are the distance and force between atoms α and β, respectively; and Ω^{α} is the atomic volume of atom α. Once the stress on each atom was computed, we then averaged the stress over the entire sheet every 500 MD time-steps, and averaged these values over the latter half of the relaxation period of 10000 time-steps in order to obtain both a spatial and temporal average of the stresses. This method provides a single stress value for every strain increment, thereby allowing us to construct a stress-strain curve for the graphene sheets.

The inter-atomic potential and simulation method as a whole were validated by deforming pristine graphene and comparing the results to experiments. Our methods predicted an elastic modulus of $0.8TPa$, an ultimate strength of $125GPa$, and a strain-at-failure of 25% for zig-zag oriented graphene. Our predicted value of elastic modulus is within 20% of the experimental value reported by Lee *et al.* (*6*), while the ultimate strength and strain at failure match the experimental values.

The first-principles density functional theory (DFT) calculations were performed with a plane-wave basis-set using the ab initio simulation package, VASP (*7, 8*). Projector-augmented wave potentials (PAW) (*9*) were used to represent the ionic cores, and Perdew-Burke-Ernzerhof (PBE) exchange-correlation functionals (*10*) were used for gradient approximations. For all the DFT calculations, a vacuum of 12Å was used in the direction perpendicular to the graphene sheets, and the sheets were periodic in the direction parallel to the grain boundaries (the Y-direction). In the X-direction, we saturated the non-periodic graphene edges with hydrogen atoms in order to ensure that all carbon atoms were sp^2 bonded (the Z-direction is normal to the graphene basal-

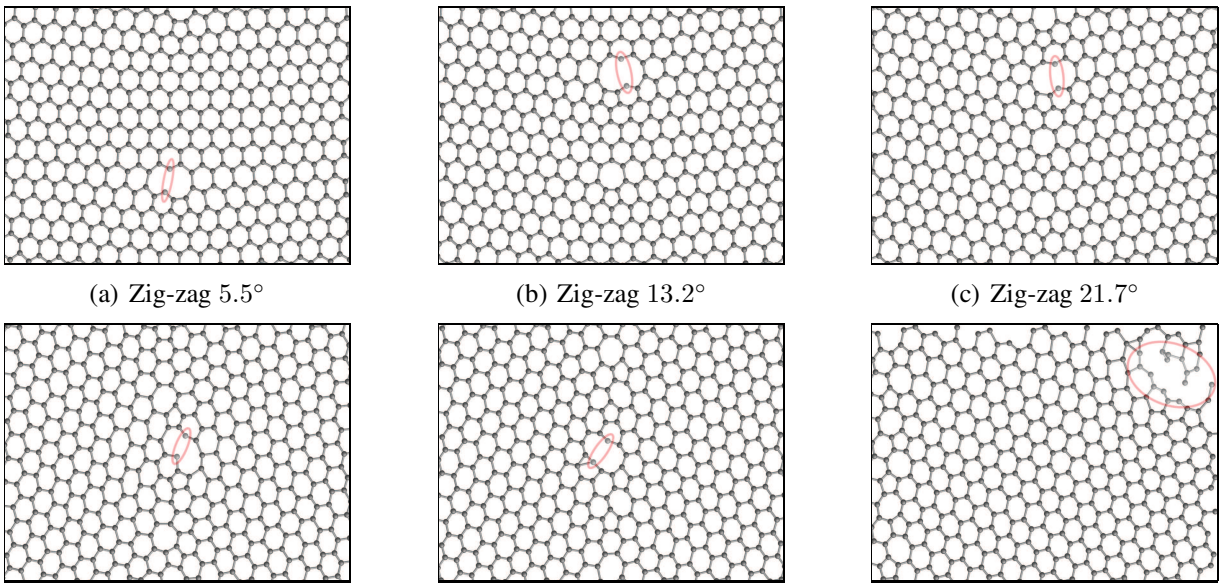
plane). A kinetic energy cutoff of 500eV was used in all DFT calculations. The structures were relaxed using the conjugate-gradient algorithm until the atomic forces were smaller than 0.04eV/Å. A convergence study was performed in which the k-point mesh was varied from $1 \times 5 \times 1$ up to $1 \times 20 \times 1$, with the key results varying by no more than 0.2% (only 1 k-point has been used in the Y- and Z-directions since they are both non-periodic). A separate study was also carried out in which the width of the model (in the X-direction) was varied from 18.7Å to 28.9Å; in this case, the maximum discrepancy in the results was less than 1%.

2 Figures



(a) Zig-zag (b) Arm-chair

Figure 1: The stress-strain curves of zig-zag (a) and arm-chair (b) oriented graphene sheets pulled parallel to the grain boundaries.



(a) Zig-zag 5.5° (b) Zig-zag 13.2° (c) Zig-zag 21.7°

(d) Arm-chair 15.8° (e) Arm-chair 21.4° (f) Arm-chair 28.7°

Figure 2: The initial stages of failure in zig-zag (a-c) and arm-chair (d-f) oriented graphene sheets pulled parallel to the grain boundaries.

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