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Engelund, Mads; Fürst, Joachim Alexander; Jauho, Antti-Pekka; Brandbyge, Mads

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Localized Edge Vibrations and Edge Reconstruction by Joule Heating in Graphene Nanostructures

M. Engelund,^{1,*} J. A. Fürst,¹ A. P. Jauho,^{1,2} and M. Brandbyge¹

¹*DTU Nanotech, Department of Micro and Nanotechnology, Technical University of Denmark (DTU), Ørstedsgade, Building 345E, DK-2800 Kongens Lyngby, Denmark*

²*Department of Applied Physics, Helsinki University of Technology, P.O. Box 1100, FI-02015 TKK, Finland*
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Control of the edge topology of graphene nanostructures is critical to graphene-based electronics. A means of producing atomically smooth zigzag edges using electronic current has recently been demonstrated in experiments [Jia *et al.*, *Science* **323**, 1701 (2009)]. We develop a microscopic theory for current-induced edge reconstruction using density functional theory. Our calculations provide evidence for localized vibrations at edge interfaces involving unpassivated armchair edges. We demonstrate that these vibrations couple to the current, estimate their excitation by Joule heating, and argue that they are the likely cause of the reconstructions observed in the experiments.

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Graphene, a single sheet of carbon atoms in a hexagonal lattice, is a material currently under intense scrutiny [1,2]. Graphene is interesting not only because of its exotic material properties, but even more so due to its potential use in future electronic components. Graphene electronics has a tremendous potential [3,4], but its practical realization requires the ability to manufacture graphene nanostructures in a controlled and efficient manner. The topology of graphene edges plays a fundamental role in determining the electronic and transport properties of these devices [5–7]. Thus, the control and stability of edges is crucial for further development of graphene-based electronic devices. Recent experiments [8,9] show that simple armchair and especially zigzag edges are the most commonly occurring edge structures and that their formation and dynamics are strongly influenced by the energetic electrons in a transmission electron microscope (TEM). However, intermediate reconstructed forms also exist [10,11]. In an important recent experiment, Jia *et al.* [12] demonstrated the formation of smooth zigzag edges from disordered edges in graphene in the presence of an electronic current. The possibility of an *in situ* fabrication process, as suggested by this experiment, is very attractive. However, at the same time the devices should remain stable in the presence of electrical current for reliable operation, further underlining the importance of understanding the microscopic edge reconstruction mechanisms.

In this Letter, we present an *ab initio* study of current-induced edge reconstructions in systems, where armchair and zigzag edges are adjacent. As the first example, consider the graphene nanoribbon (GNR) junction shown in Fig. 1. A zigzag GNR to the left is connected to a wider zigzag GNR to the right by an armchair edge (ZAZ structure). Note that the edges are not passivated (we return to this point below). The second example is a ZAZZZ system (see Fig. 2) where an extra zigzag edge is inserted. These

two structures are chosen to mimic the experimental situation and to test the generality of the trends found in our calculations.

Using density functional theory (DFT) [13,14], we shall demonstrate that strong local Joule heating occurs in systems of this kind for voltage biases and currents of the same order of magnitude as in the experiment by Jia *et al.* [12]. In order to have significant Joule heating, two conditions are of importance. First, localized vibrations are necessary in order to spatially concentrate the energy. Second, the electronic subsystem must couple strongly with the local vibrations and be locally out of equilibrium in order to provide energy to the vibrations. As we shall show, the structures shown in Figs. 1 and 2 indeed exhibit localized vibrational modes. These modes originate from “armchair dimers,” defined as C-C dimers coordinated in the same way as the outermost atoms of a nonpassivated armchair edge. In what follows, we call these modes “armchair dimer modes” (ADMs). Next, we show that zigzag-armchair junctions exhibit strong local scattering of the current carrying electrons such that we can expect a local voltage drop across the junction. Finally, we estimate the heating of the ADMs in the two model systems and argue that the heating of the ADMs is the likely cause of the reconstruction of the edges observed in the experiment by Jia *et al.* [12].

Let us now quantitatively address the existence of localized vibrational modes in systems with mixed zigzag and armchair edges. Using finite displacement calculations [15], we find two such modes (see Fig. 1) for the ZAZ system with a vibrational energy of ~ 250 meV. These modes are strongly localized to the outermost atoms of the armchair edge: already for nearest neighbors, the mode amplitude has dropped by $\sim 85\%$. The modes are truncated versions of the vibrational edge states that give rise to the quasi-1D band in the density of states (DOS) [17] of the

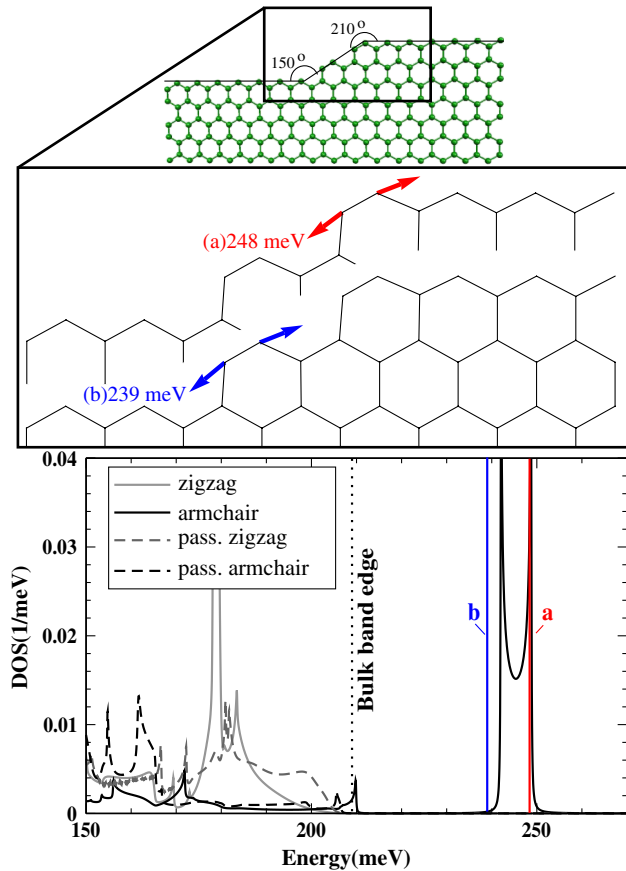


FIG. 1 (color online). (Top) The ZAZ structure. (Middle) The two modes lying outside of the bulk bands, labeled (a) and (b), respectively. Atomic displacements of less than 5% of the total amplitude are not shown. (Bottom) The energies of the two localized modes compared with the local vibrational DOS of the outermost carbon atoms on infinite graphene edges. For H-passivated edges, additional 1D bands are found at ~ 380 meV (not shown).

infinite armchair edge (full black curve in Fig. 1, see also Ref. [18]). These two ADMs are energetically localized since both the infinite zigzag edges (full grey curve in Fig. 1) and bulk graphene (band edge shown as a dotted line) have a vanishing DOS above ~ 200 meV and thus cannot cause energy broadening above this energy in the harmonic approximation. The modes outside of the bulk band are only broadened by interactions with electrons and, at high temperature, by anharmonic interactions.

For the ZAZZZ system, we identify three localized modes (Fig. 2) which again involve 2-coordinated armchair dimers. For this case, the vibration amplitude is significant not only on the armchair edges but also at the 240° ZZ edge.

Hydrogen passivation is predicted to play a role for the edge structure [19]. However, we expect the ADMs to be localized even if they are adjacent to hydrogen-passivated edges. We find that the passivated zigzag and armchair edges do *not* have vibrations with energies ~ 250 meV in

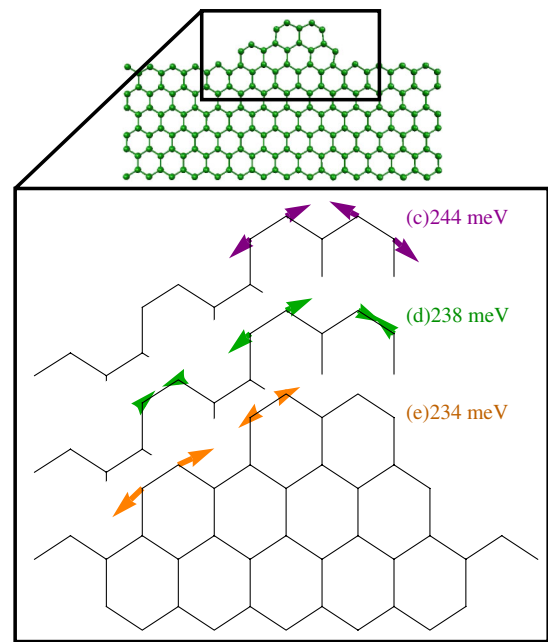


FIG. 2 (color online). (Top) The ZAZZZ structure. (Bottom) The three ADMs, labeled (c), (d), and (e), respectively. Atomic displacements of less than 5% of the total amplitude are not shown.

their DOS (dashed black and grey curves in Fig. 1, respectively), in agreement with the empirical-potential calculation in Ref. [20], and thus cannot provide harmonic damping. We constrain our studies to nonpassivated edge interfaces since there were no signs of hydrogen playing a role in the experiments by Jia *et al.* [12], and we also expect hydrogen to desorb at much lower temperatures than where the breaking of carbon-carbon bonds takes place. The barrier for hydrogen desorption from an armchair edge is lower compared to that of the outermost C-C unit, 4 eV (Ref. [21]) and 6.7 eV (Ref. [12]), respectively.

In addition to the existence of localized vibrational modes, the occurrence of local Joule heating also requires local scattering of electrons. By DFT transport calculations [14,22,23], we find that the scattering states localized at the zigzag edge are interrupted at the zigzag-armchair junction, illustrated by the square modulus of the transmitting electronic scattering states (eigenchannels [24]) at the Fermi level, shown for the minority spin in Fig. 3. Reference [25] shows, by extensive tight-binding calculations, that scattering can in general be expected at armchair-zigzag edge interfaces and that scattering increases with the length of the armchair edge. Since the same behavior is predicted for different systems with two different methods (*ab initio* versus tight binding), it seems that backscattering at armchair-zigzag interface is indeed a generic feature of these systems.

We next estimate the heating of the ADMs in the two model systems. If the anharmonic couplings are neglected, the mean steady-state occupation, $\langle n^\lambda \rangle(V)$, can be calcu-

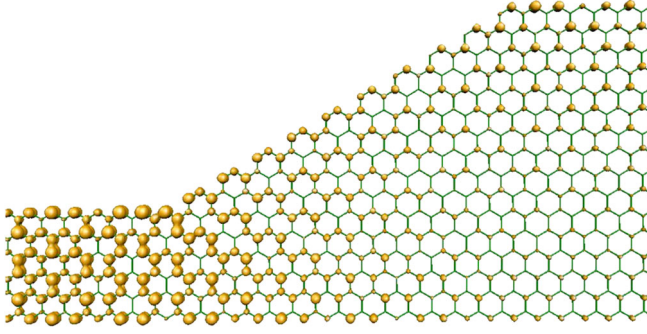


FIG. 3 (color online). The absolute square of the minority spin left-to-right scattering states at the Fermi level for a large ZAZ system, corresponding to a transmission of 0.15.

lated from the ratio of the current-induced phonon emission rate, $\gamma_{\text{em}}^\lambda(V)$, and the effective phonon damping rate, $\gamma_{\text{damp}}^\lambda(V)$ (here V is the voltage drop across the scattering region). Since the investigated modes lie outside the vibrational bulk band, the damping due to the bulk phonon reservoir vanishes. Assuming zero electronic temperature and energy-independent scattering states within the bias window, the emission rate is [16,26]

$$\gamma_{\text{em}}^\lambda(V) = \frac{eV - \hbar\omega_\lambda}{\hbar\pi} \theta(eV - \hbar\omega_\lambda) \text{Tr}[\mathbf{M}^\lambda \mathbf{A}_L \mathbf{M}^\lambda \mathbf{A}_R]. \quad (1)$$

Here, $\hbar\omega_\lambda$ is the vibrational energy of mode λ , \mathbf{M}^λ is the coupling of the mode to the electronic degrees of freedom calculated by finite difference techniques, and $\mathbf{A}_{L/R}$ is the electronic spectral density of left or right moving electrons, evaluated at the Fermi level by DFT transport calculations [14,22,27]. The rate $\gamma_{\text{damp}}^\lambda(V)$ is [16]

$$\gamma_{\text{damp}}^\lambda(V) = \frac{\omega_\lambda}{\pi} \text{Tr}[\mathbf{M}^\lambda \mathbf{A} \mathbf{M}^\lambda \mathbf{A}], \quad (2)$$

where $\mathbf{A} = \mathbf{A}_L + \mathbf{A}_R$ is the total electronic spectral density at the Fermi level. The occupation $\langle n^\lambda \rangle(V)$ becomes

$$\langle n^\lambda \rangle(V) = \frac{1}{2} \theta(eV - \hbar\omega_\lambda) \left(\frac{eV}{\hbar\omega_\lambda} - 1 \right) s^\lambda, \quad (3)$$

where $s^\lambda = \frac{2 \text{Tr}[\mathbf{M}^\lambda \mathbf{A}_R \mathbf{M}^\lambda \mathbf{A}_L]}{\text{Tr}[\mathbf{M}^\lambda \mathbf{A} \mathbf{M}^\lambda \mathbf{A}]}$ is a dimensionless heating parameter that can vary from 0 (no heating) to 1 (maximal heating). By assuming that $n^\lambda(V)$ is Bose distributed, one can extract an effective temperature of the mode, $T_{\text{eff}}^\lambda(V)$, which we plot in Fig. 4 for the localized modes identified in Figs. 1 and 2. The calculated electronic damping rates and heating parameters are shown in Table I.

The mode temperatures should be compared to the uniform temperature, T_d , needed to destabilize the system on a time scale relevant to the experimental conditions, which we judge to be of the order of seconds. Thus, we consider a corresponding rate of desorption of carbon dimers, $q \sim 1$ Hz. We estimate $T_d \sim 2500$ K (see Fig. 4)

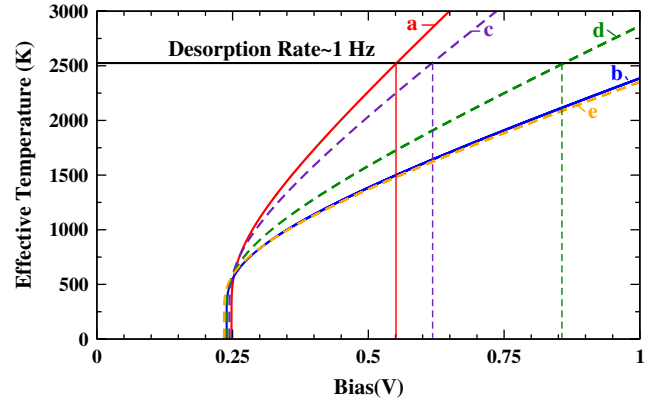


FIG. 4 (color online). The effective temperature as a function of bias for the localized modes for the ZAZ (full curves) and the ZAZZZ system (dashed curves). The horizontal line indicates the uniform temperature where the decay rate of the outer C-C dimer of an armchair reaches 1 Hz.

using the Arrhenius equation, $q = \nu \exp[-E_a/(k_B T_d)]$, a characteristic attempt frequency $h\nu = 100$ meV (a typical phonon frequency), and an activation energy $E_a = 6.7$ eV [12].

We can compare the heating of the localized ADM to the modes inside of the bulk band by calculating their harmonic damping due to their coupling to the bulk phonons [28] and adding this to the damping by the electrons. We find that this damping is 1–100 times the damping due to the electronic couplings leading to temperatures typically below 1000 K even for a bias of 1 V. Since this temperature yields desorption rates much lower than those seen in the experiments, we conclude that the Joule heating of the harmonically damped modes cannot account for the reconstruction. In contrast, as Fig. 4 shows, the ADMs reach a high temperature at much lower biases and can thus provide a channel for local desorption. Furthermore, these modes are also more likely to be involved in the desorption since they directly involve the desorbing dimers.

A quantitative comparison with experiments would require a much more sophisticated theory, which is beyond the scope of this Letter. For example, one should consider the anharmonic coupling of ADMs and evaluate the non-equilibrium electronic distribution function from which the actual potential profile in the sample can be extracted.

TABLE I. Mode characteristics.

Mode	$\hbar\omega_\lambda$ (meV)	$\hbar\gamma_{\text{damp}}^\lambda$ (μeV)	s^λ
ZAZ, (a)	248	99	0.77
ZAZ, (b)	239	63	0.29
ZAZZZ, (c)	244	19	0.63
ZAZZZ, (d)	238	26	0.38
ZAZZZ, (e)	234	64	0.28

Finally, let us investigate the role of different types of edge interfaces. Figure 1 shows two examples: a 150° zigzag-armchair interface and a 210° armchair-zigzag interface. Intuitively one would expect the 2-coordinated dimer directly at the 210° corner to make this interface especially prone to reconstructions. This is confirmed by our calculations of their heating: we find that the 210° modes [modes (a), (c), and (d)] exhibit markedly stronger heating than modes associated with the 150° corner, the reason being their stronger coupling to the current carrying electrons (s^λ closer to 1 for these modes). This scenario is consistent with two experimental observations by Jia *et al.* [12]. First, they observe that a 150° interface survives even after massive reconstruction has occurred [Fig. 2(D) of Ref. [12]]. Second, certain armchair edges evaporate while others grow longer. The theory outlined here predicts that the evaporating armchair edges are the ones bordered by at least one 210° junction. Conversely, zigzag edges and armchair edges bordered by 150° junctions would be the stable edges and would grow as the unstable armchair edges evaporate.

In conclusion, we have demonstrated how specific C-C dimers can play a fundamental role in current-induced reconstruction in graphene systems with mixed edges. We show that these dimers give rise to spatially and energetically localized modes, which give a natural explanation for the low onset bias for reconstruction observed in the experiments [12]. Identifying the modes that heat up also allows us to make predictions of the overall behavior of a graphene sample under the influence of a current. Specifically, we predict that zigzag-armchair junctions with an angle of 150° would be more stable than the junctions with a 210° angle. We believe reasoning along these lines could contribute towards a quantitative understanding of other intriguing edge structures, e.g., the zigzag reczag discussed recently in Ref. [11].

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*mads.engelund@nanotech.dtu.dk

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