

Supplementary Information:
**Current-induced changes of migration energy barriers in carbon
based systems**

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ORIGINS OF THE CURRENT-INDUCED FORCES

Here we give a short intuitive description for the origins of the current induced forces in DFT-NEGF simulations, of their non-conservativeness, and of the involved approximations.

In general, when current flows through a system and gets scattered at an obstacle, there will usually be an accumulation of electrons on the side of the obstacle closer to the electrode with the higher chemical potential, and a depletion of electrons on the opposite side. In a classical picture the positive nucleus of such an obstacle (adatom in our case) will then be attracted to the side with the negative charge (where electrons accumulate), which results in a net current induced force, and which in this case points against the current flow. More generally the finite bias leads to depopulation of some of the states in the junction, and increased population of other states. Such a change of orbital populations leads to a general change of the forces, which can point in any direction, and will depend on the system. All these combined effects lead to forces in x , y , and z direction, and are the origin of the phenomenon of electromigration.

In the main manuscript we show that for a realistic system of a C adatom moving on a CNT such forces are not conservative. In an intuitive picture, the nonconservativeness of the forces arises since the current densities in the system are not homogeneous. If for example an adatom moves against the current flow along bonds with high current density, and assuming that the current flow is along positive z , while the current-induced forces point towards $-z$, then it will typically gain a large amount of energy by the current-induced force. We can then move the atom along a path perpendicular to the current flow to a part of the system with a smaller current density. We then move it back to its original z coordinate along this path with low current density, and where typically the current-induced forces are reduced. The energy loss will then be smaller than the energy gain we obtained when moving the atom towards smaller z . Note that even if the forces have x and y components, the work involved in the motion of the adatom perpendicular to the current flow cancels over a closed path, if we consider a structure that is periodic along z . Following a closed path we can therefore obtain a non-zero net work, which means that the forces are non-conservative. We demonstrate this in Fig. 5 of the main manuscript, where moving the adatom against the current flow along one path (A1), and back on another path (A2→A3), a net work is done on the adatom.

We conclude by pointing out the restrictions of the used DFT-NEGF method. The main approximation is that we assume that the motion of the atoms is always quasi-static. This corresponds to neglecting the momentum transfer from the flowing electrons to the nuclei, and considering only the forces arising from the changes in electrostatic and chemical bonding energies. This implies that we do not consider current-induced heating effects, which would lead to vibrations (motion) of the atoms around the lowest energy path.

CARBON ADATOM MIGRATION ON CNT

For the C adatom moving on graphene and the CNT, we present the forces as function of voltage for three different beads along the A1 path (Fig. 1). For both graphene and the CNT the forces change significantly in the considered bias range, up to about $0.5 \text{ eV}/\text{\AA}$.

Figure 2 shows the work profile for path A2 in the CNT at varying V_b . We find a notable reduction of the barrier height together with a more and more negative total work as the bias increases.

In order to verify that our findings are generally applicable for different types of metallic CNTs, we consider metallic CNTs with different chiralities, namely (6,3) and (7,4), see Fig. 3. The direction of the path is different for the different chiralities, so that also the 0 bias energy profile is different. For the path used for the (6,3) chirality the 0 bias barrier height is 0.39 eV and, and for the (7,4) chirality it is 0.14 eV . For the (6,3) and (7,4) chiralities we find that the barrier height is reduced by about 0.35 and 0.18 eV , respectively, at 1.6 V . These results show that qualitatively the current-induced energy barrier suppression is analogous for all considered CNTs, and differ only on a quantitative level, which shows that our results are generally valid for different types of CNTs.

Finally in Fig. 4 we show the current-induced forces over the migration path at a bias of 1.6 V for two different lengths of the considered scattering region. The forces are essentially identical, showing that the results are not dependent on the length of the scattering region considered in our calculations. This also confirms that the forces are predominantly current-induced, while the field induced components are small.

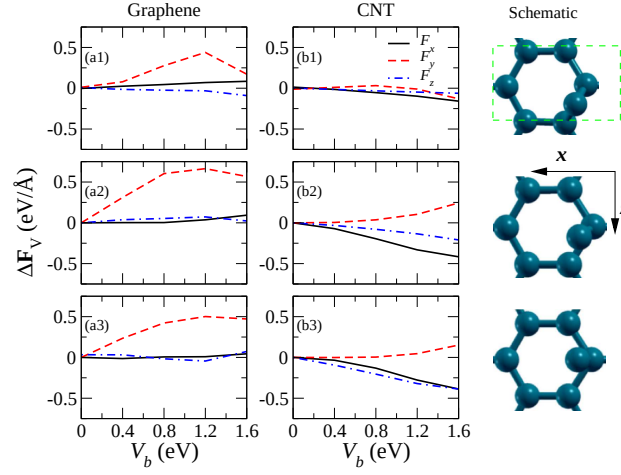


FIG. 1: Current-induced forces, $\Delta\mathbf{F}_V = \mathbf{F}(V) - \mathbf{F}(V = 0)$, on the adatom adsorbed on graphene and the CNT for the beads with indices 0, 2, and 4. Results for graphene are shown in the left column, and those for the CNT in the right column. The positions of the adatom in the three beads are illustrated on the side panels.

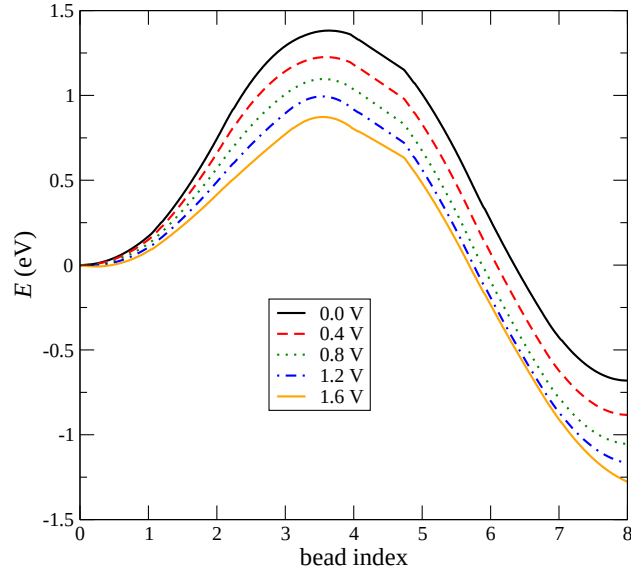


FIG. 2: NEB profile under bias for the migration of the C adatom on a (5,5) CNT through path A2.

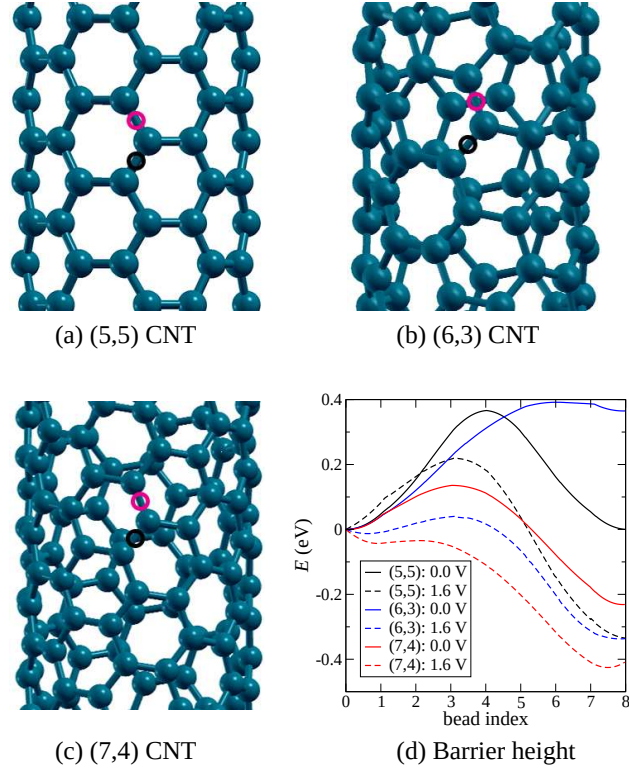


FIG. 3: (Color online) Energy barriers at 0 and 1.6 V, for a (5,5), a (6,3), and a (7,4) CNT. The reduction of the barrier is qualitatively similar for the (5,5), (6,3), and (7,4) CNT. The migration path is from A to B (against the flow of current). Solid lines represent the 0.0 V and dashed line for the 1.6 V barrier heights. The end-point atomic structures of the migration paths are indicated for the three considered chiralities, where the pink circle corresponds to the bead with index 0, and the black circle represents the bead with index 8.

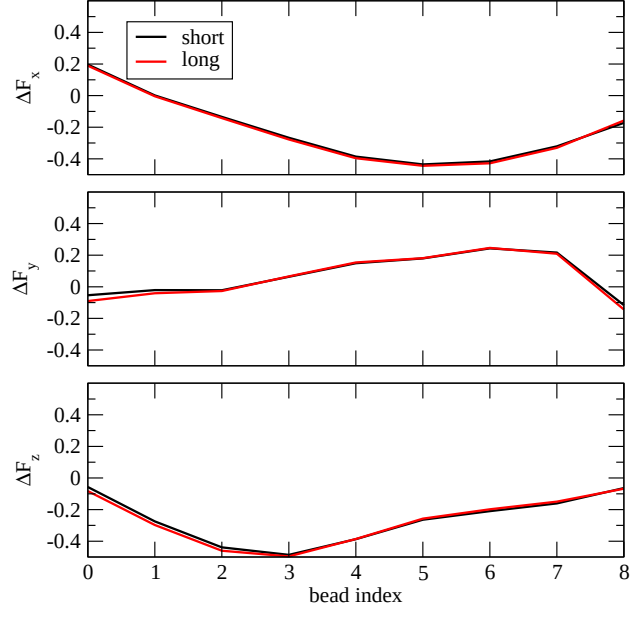


FIG. 4: Current-induced forces on the adatom attached to a CNT kept at 1.6 V for two lengths of the scattering region, 39.9 Å (short) and 79.8 Å (long), as function of the bead index.

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