

Width Influence on the Polaron Dynamics in Graphene Nanoribbons

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INTRODUCTION

Carbon-based nanomaterials¹⁻⁴ are recognized as promising solutions to the development of novel electronic devices that present smaller environmental impact when compared to its inorganic counterparts. Due to unique features such as easy of synthesis, strict two-dimensionality, low cost, and high mechanical strength graphene has attracted huge interest to the design of photovoltaic⁵, energy storage⁶, and field-effect transistor applications. Significant efforts have been performed theoretically⁷ and experimentally⁸ in order to understand the charge transport mechanism in graphene sheets and nanoribbons. Importantly, these works have investigated the charge transport from the framework of metallic-like behavior⁸⁻¹². Nonetheless, theoretical studies considering the semiconducting-like physical picture for charge transport mechanism, to describe the system features which may affect the polaron dynamics, are still insufficient.

In this work, the influence of the nanoribbon width on the dynamics of polarons in armchair graphene nanoribbons (GNRs) is numerically investigated in the scope of a two-dimensional Su-Schrieffer-Heeger model with lattice relaxation. The results show that the polaron dynamics changes substantially varying the nanoribbon width. Moreover, the interplay between external electric field and the electron-phonon coupling plays the role of drastically modifying the charge localization through the nanoribbon and, consequently, the polaron dynamics. This investigation may enlighten the understanding of the charge transport mechanism in graphene-based nanomaterials.

METHODS

In order to describe the charge transport in GNRs we developed a two-dimensional version of

the Su-Schrieffer-Heeger (SSH) model¹², modified to include an external electric as follows

$$H_{elec} = - \sum_{\langle i,j \rangle, s} (t_{i,j} C_{i,s}^\dagger C_{j,s} + h.c.) + \sum_{\langle i,j \rangle} \frac{K}{2} y_{i,j}^2 + \sum_{\langle i,j \rangle} \frac{p_i^2}{2M}$$

where $\langle i,j \rangle$ denotes summing over nearest neighbor sites i and j . For the electronic part, the operator $C_{i,s}^\dagger$ ($C_{j,s}$) creates (annihilates) a π -electron with spin s at the i th site. $t_{i,j} = \exp[-i\gamma A(t)\delta](t_0 - \alpha y_{i,j})$ is the hopping integral, where t_0 denotes the hopping of a π -electron between neighboring sites with no field present in an evenly spaced lattice, α is the e-ph coupling constant, and $y_{i,j}$ is the relative displacement coordinate between neighboring sites. The electric field $E(t)$, which was turned on adiabatically according to reference¹³ in order to avoid numerical errors, is included in our model by means of the time-dependent vector potential $A(t)$ through a Peierls substitution of the phase factor to the hopping integral. This is the simplest way of implementing electric fields consistently with periodic boundary conditions. $\gamma \equiv ea/(\hbar c)$, with a being the lattice parameter, e the absolute value of the electronic charge, and c the speed of light.

The lattice backbone dynamics is treated with a classical approach by means of a Newtonian equation $M\ddot{u}_n = F_n(t)$. Here, $F_n(t)$ represents the force experienced by a particular carbon atom n . The force expression is analogous to that originally developed by Silva and co-workers¹³. Moreover, this equation can be numerically integrated according the methodology described in reference¹³. The electron dynamics is obtained by solving the time-dependent Schrödinger equation (TDSE). The wave functions are constructed by means of a linear combination of instantaneous

eigenstates. Thus, the solutions of the TDSE can be expressed as

$$\psi_{k,i}(t + dt) = \sum_l \left[\sum_m \phi_{l,m}^*(t) \psi_{k,m}(t) \right] \times \exp(-i\varepsilon_i dt/\hbar) \phi_{l,i}(t)$$

in which $\{\phi_{l,i}(t)\}$ and $\{\varepsilon_i\}$ are the eigenfunctions and the eigenvalues of the Hamiltonian at a given time t , respectively. In this work, we have adopted the following values for the constants, $t_0 = 2.7$ eV and $K = 57$ eV/Å². The e-ph coupling α is in the range from 3.5 to 10 eV/Å, which according to the literature corresponds to suitable values for GNRs. This range for α is in very good agreement with values obtained in experimental studies for graphene^{8,10,12}, which are 6.0 eV/Å, if the e-ph coupling mechanisms other than the bond stretching can be neglected. Moreover, the energy band gaps obtained in our study are also in agreement with the band gap energies for GNRs obtained through electronic structure calculations.

RESULTS AND DISCUSSION

As a starting point of our investigations, we have studied the behavior of the band gap value as a function of the e-ph constant and the GNR width. The results presented in Figure 1 are in very good agreement with earlier studies, which justifies the method used in this work. In the following, we restrict our studies of the features of the polarons to the parameter space that gives finite band gaps. In particular, from the two possible families of GNR widths, that is, $2p$ and $2p+1$, we limit the discussion here to the $2p$ family ($n = 4, 6, 8,$ and 10) because the band gap of the $2p+1$ family is essentially zero and no polaron solution is possible.

We now turn to results concerning the polaron dynamics in GNRs. Figure 2 shows the actual path of a polaron through an armchair GNR with width $n = 4$ and with periodic boundary conditions. The e-ph coupling constant is set to 5.0 eV/Å, and the external electric field is 1.0 mV/Å, applied in the direction along the nanoribbon. It is important to note that the hexagonal grid presented in the figure is a mere representation of the GNR structure. Therefore, one should take the charge disposition over bondless regions of the ribbon as a qualitative pattern. Two interesting properties stand out in the polarons

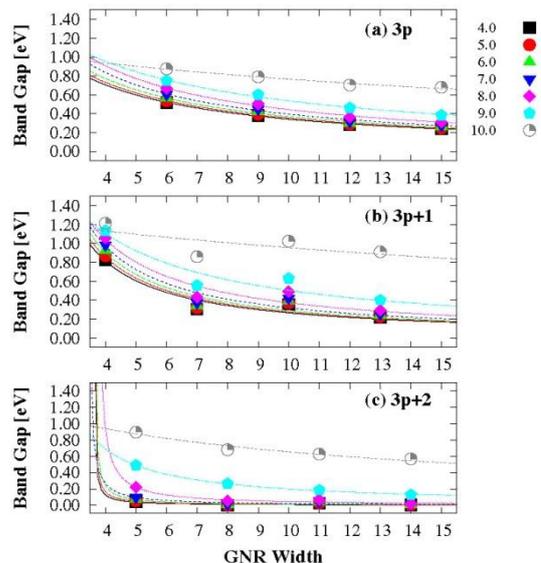


Figure 1. Different band gap regimes as a function of the GNR widths for several different electron–phonon coupling strengths considering the (a) $3p$, (b) $3p+1$, and (c) $3p+2$ families.

dynamics of Figure 4. First is the delay in the polaron response to the applied electric field, and second is the difference between the initial and the steady-state extension of the polaron. Naturally, these two features are connected and have to do with the aforementioned two-fold role the electric field plays in polaron dynamics for GNRs. The electric field initially plays the role of assisting the charge localization in order to create a stable polaron; it is only after this task is accomplished that the collective behavior is fully manifested as the movement through the lattice. Therefore, we can conclude that the applied electric field favors the polaronic charge density profile presented in Figure 2.

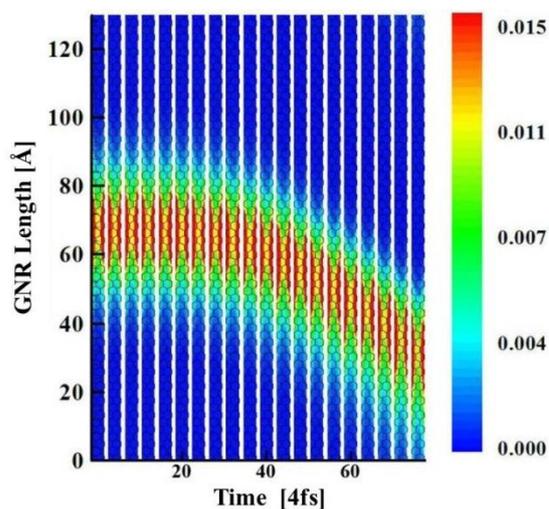


Figure 2. Polaron dynamics in an $n = 4$ width armchair nanoribbon subjected to an electric field of $1.0 \text{ mV/\text{Å}}$.

CONCLUSIONS

In summary, we have performed a systematic numerical study on the polaron dynamics in armchair GNRs by means of a two-dimensional tight-binding model with lattice relaxation. By comparing different GNR widths, we could determine the critical conditions for a polaron transport to take place. Moreover, our methodology was able to accurately predict the band gap dependence on the width of the GNRs as well as their values. A careful investigation on the velocity regimes of polarons was also performed. We observed that electric fields favor the occurrence of supersonic polarons.

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