

Polaron Induced Deformations in Carbon Nanotubes

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We compute for the first time full elastic deformations, as well as length, of self-trapped electronic states in carbon nanotubes of general radius and chirality, within the unifying framework of a recently introduced two field model for electromechanics of carbon nano-structures. We find that deformations are highly non monotonic in the chiral angle, whereas the length of the polaron is not. Applications include nano-mechanical devices as electrically or optically driven nano-actuators.

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Coupling between electronic and elastic structure of carbon nanotubes [1–3] leads to theoretically interesting and technologically relevant phenomena: among other things, gap opening can be induced via strain [4, 5] (allowing mechanical control of the conductance) and injecting electron/holes induces mechanical deformations [6, 7] (important for realization of electrical nano-actuators) or shifts in Raman phonon modes [8–10]. Novel excitations leading to spontaneous distortions driven by electron-phonon couplings are of particular interest to the electromechanics of nano devices [11, 12]. In particular light induced mechanical deformations, or optomechanical effects can be observed at high temperatures in nanotube, as excitons are more strongly bound [13]. Recently, Verissimo-Alves *et al* [14] have predicted the existence of self-trapped electron and hole states in semiconducting carbon nanotubes by feeding parameters from *ab initio* density functional calculations into a very simplified continuum model. They obtained polaron lengths of the order of 40-60 nm and energies of order of 10^{-2} meV. Their long polaron approximation is confirmed by a recent atomistic numerical analysis: Bratek *et al* [15] found that the azimuthal dependence becomes relevant only at very high electron-phonon couplings, for which the long polaron approximation fails, and the electron localizes on a few unit cells. For actual carbon nanotubes, they found that the self-trapped electronic states resemble the nonlinear long Schrödinger soliton which Verissimo-Alves employed as a model.

It is important, both theoretically and technologically, to be able to predict exactly which kind of deformations can be induced by these kind of excitations, and in the general case. Yet, the Verissimo-Alves simplified continuum model cannot address the complex deformations in carbon nanotubes: it completely ignores chirality dependence and neglects to account for torsional deformations or inner displacements. Indeed traditional analytical continuum approaches employed in the treatment of carbon nanotubes [1, 2, 16, 17] cannot describe atomistic structure without ad hoc phenomenological extensions [7, 18, 19]. On the other hand, more complete treatments based on atomistic models are too complex

to be solved analytically or to return detailed answers for a general case: Bratek *et al* for instance only address polarons in zigzag nanotubes.

In this letter we employ a recently introduced bicontinuum model to solve this predicament and calculate the full range of deformations induced by self-trapped electrons/holes for the general carbon nanotube.

In a recent work, Nisoli *et al* [20] have introduced a two field unifying framework for elasticity, lattice dynamics and electromechanical coupling in carbon nanostructures that accounts for the full atomistic detail of the graphenic lattice, and explains a wealth of experimental and numerical results without computationally intensive atomistic treatments. They defined an elastic field for each of the mutually interlaced triangular sublattices that make the honeycomb lattice, $u^i(x)$, $v^i(x)$, $i = 1, 2$ (see Fig. 1) and the corresponding strain tensors [21] $u^{ij} = \partial^{(i} u^{j)}$, $v^{ij} = \partial^{(j} v^{i)}$, and wrote the elastic energy via considerations of symmetry. Unlike Ref. [20], we work here with the average displacement $2p^i = (u^i + v^i)$, inner displacement $2q^i = (u^i - v^i)$, and corresponding strain tensors p^{ij} , q^{ij} . In these new variables, the elastic energy of Ref. [20] becomes $W_{\text{el}} = \int \sigma V_{\text{el}}[p, q] dx^2$, with

$$V_{\text{el}}[p, q] = \hat{\mu} p^{ij} p_{ij} + \frac{\hat{\lambda}}{2} p_i^i p_j^j + \frac{1}{2} \omega_{\Gamma}^2 q^2 - 2\beta e_{ijk} q^i p^{jk}, \quad (1)$$

where we have employed the long polaron approximation to neglect the dispersion of the optical branches [26]. The tensor e_{ijk} is invariant under the C_{3v} group and can be represented by the three unit vectors $\{\hat{e}^{(l)}\}_{l=1,3}$ of Fig. 1,

$$e_{ijk} = \frac{4}{3} \sum_{l=1}^3 \hat{e}_i^{(l)} \hat{e}_j^{(l)} \hat{e}_k^{(l)}. \quad (2)$$

There are thus 4 parameters: ω_{Γ} , the graphite-like optical frequency; β which determines the strength of the rotational symmetry breaking, contains all information about the point group symmetry of graphene, and defines the important length $\ell \equiv 4\beta/\omega_{\Gamma}^2 = 0.3$ [20]; and the generalized Lamè symbols $\hat{\mu}$, $\hat{\lambda}$, which can be expressed

in terms of the longitudinal and transverse speed of sound in graphene, $v_L^2 = 2\hat{\mu} + \hat{\lambda} - 4\beta^2/\omega_F^2$, $v_T^2 = \hat{\mu} - 4\beta^2/\omega_F^2$, and are related to the actual Lamé symbols of graphene μ_r , λ_r via $\mu_r = \hat{\mu} - 4\beta^2/\omega_F^2$ and $\lambda_r = \hat{\lambda} + 4\beta^2/\omega_F^2$. We then write p in term of the isotropic (γ_o), anisotropic (γ), and shear/torsional (η) strain in the nanotube coordinates

$$\begin{cases} p^{\phi\phi} = \gamma_o + \gamma \\ p^{zz} = \gamma_o - \gamma \\ p^{\phi z} = p^{z\phi} = \eta \end{cases} \quad (3)$$

In these new variables the elastic energy (1) now reads

$$\begin{aligned} V_{\text{el}} = & 2\hat{\lambda}\gamma_o^2 + 2\hat{\mu}(\gamma_o^2 + \gamma^2 + \eta^2) + \frac{1}{2}\omega_F^2 q^2 \\ & - 4\beta q^\phi(\gamma s_3 - \eta c_3) + 4\beta q^z(\gamma c_3 + \eta s_3). \end{aligned} \quad (4)$$

(We have shortened $c_3 \equiv \cos(3\theta_c)$, $s_3 \equiv \sin(3\theta_c)$, θ_c is the chiral angle of the nanotube, and used $e_{\phi,\phi,\phi} = -e_{\phi,z,z} = -s_3$, and $e_{z,z,z} = -e_{\phi,\phi,z} = -c_3$.)

As explained in Ref. [20], one can simply “wrap around” the elastic energy of graphene to deal with carbon nanotubes. In the cylindrical geometry, with coordinates $\{r, \phi, z\}$ of Fig. 1, a minimal coupling between the tangential displacements p^i and the radial p^r appears in V_{el} of (1) via $p^{\phi\phi} = (\partial_\phi p^\phi + p^r)/r$ [21]. As explained, we assume no azimuthal dependence, and thus $2\gamma_o = (\partial_z p_z + p_r/r)$, $2\gamma = (-\partial_z p_z + p_r/r)$, $2\eta = \partial_z p_\phi$. We are neglecting the breaking of the hexagonal symmetry brought upon by the chiral vector that defines the wrapping of the carbon nanotube. This symmetry breaking *allows for new terms to be introduced in V_{el} as curvature corrections*. The parameters of our elastic energy for graphene are also corrected by curvature.

As for the low energy electronic excitations in a semi-conducting nanotube, they can be described in terms of an envelope wave-function ψ [22] of energy density

$$E_e[\psi, p, q] = -\psi^\dagger \frac{\hbar^2 \partial_z^2}{2m} \psi + E_{\text{ep}}[\psi, p, q]. \quad (5)$$

E_{ep} , the coupling between phonons and an injected electron or hole, at lowest order both in the *in-plane* elastic fields and in the electron probability density $|\psi|^2$ can be deduced via considerations of symmetry

$$E_{\text{ep}} = |\psi|^2 [\nu(q^z/e + \gamma c_3 + \eta s_3) + \nu' \gamma_o] \quad (6)$$

(e is the bond length). Physically, the term proportional to ν emerges in dielectric tubes from a deformation-induced change in the bandgap, whereas the term proportional to ν' comes from the shift in energy at the K point of the Brillouin due to second-nearest-neighbor atoms [6]. In the context of a simple tight-binding treatment [2], hopping integrals are modulated by in-plane elastic deformations. [20]: $dt^{(l)} = -\tau \hat{e}_i^{(l)} \hat{e}_j^{(l)} p^{ij} + \tau \hat{e}_i^{(l)} q^i/e$ are the three nearest-neighbor hopping integrals along the three bonds of unit vectors $\hat{e}^{(l)}$, whereas $dt'^{(l)} = -\tau' \hat{a}_i^{(l)} \hat{a}_j^{(l)} p^{ij}$

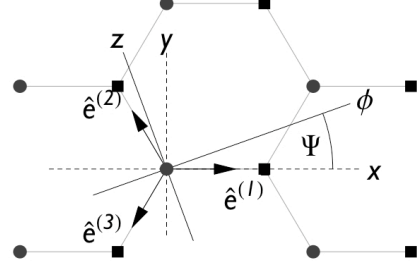


FIG. 1: The two sublattices (circles and squares) of graphene and the three unit vectors $\hat{e}^{(l)}$ used in the text. ϕ , z are cylindrical coordinates of a tube, while $\Psi = \pi/6 - \theta_c$ with θ_c the chiral angle.

are the hopping integrals along the three directions $\hat{a}^{(l)}$ of the next-nearest-neighbors. (τ , τ' are often called scaling parameters [23].) Following along the line of Ref. [5, 20], one can calculate the variation of the band gap and of the energy at the K point under strain via hopping integral modulation, and—after long yet not particularly insightful calculations—deduce (6) and in particular

$$\begin{cases} \nu' = \mp 3\tau' \\ \nu = \frac{3}{2} s_p \tau. \end{cases} \quad (7)$$

The minus sign in the first equation is for electrons, the plus for holes. Note that there is no change in sign for ν in going from holes to electrons. The other sign function is $s_1 = -1$ ($s_2 = 1$) where p is defined as a function of n , m as $p \equiv [(n-m) \bmod 3]$. This difference in sign behavior between ν and ν' was previously recognized as causing indices dependence and non monotonicity in the doping induced shift of Raman frequencies and anomalous bond contraction/expansion in zig-zag nanotubes [8–10, 20]. We will see that it controls chirality dependent expansions vs. contractions for hole or electron self-trapping.

We assume that our fields only vary along the axial coordinate z , an ansatz corroborated by previous numerical calculations, as explained above [15]. This treatment—we will see—is self consistent as it predicts very long polarons. The hamiltonian density for the entire system is then

$$\mathcal{H} = -\psi^\dagger \frac{\hbar^2 \partial_z^2}{2m} \psi + \sigma c V_{\text{el}} + E_{\text{ep}} \quad (8)$$

where V_{el} is given by (4), E_{ep} is given by (6), and $c = 2\pi r$ is the nanotube circumference. Minimization under normalization of ψ with Lagrangia multiplier ϵ_p returns the system of equations of equilibrium for our system,

$$\begin{cases} 4(\hat{\mu} + \hat{\lambda})\gamma_o = -\nu' |\psi|^2 / \sigma c \\ 4\hat{\mu}\gamma - 4\beta(q_\phi s_3 - q_z c_3) = -\nu c_3 |\psi|^2 / \sigma c \\ 4\hat{\mu}\eta + 4\beta(q_\phi c_3 + q_z s_3) = -\nu s_3 |\psi|^2 / \sigma c \\ 4\beta(\gamma c_3 + \eta s_3) + \omega_F^2 q_z = -\nu |\psi|^2 / e \sigma c \\ 4\beta(\gamma s_3 - \eta c_3) - \omega_F^2 q_\phi = 0 \\ \epsilon_p \psi = \frac{-\hbar^2}{2m} \partial_z^2 \psi + [\nu(q^z/e + \gamma c_3 + \eta s_3) + \nu' \gamma_o] \psi \end{cases} \quad (9)$$

which is linear in the elastic fields and can be solved easily for them in terms of $|\psi|^2$.

We find for the local deformation induced by an injected electron or hole the equations

$$\begin{cases} \gamma_o = \pm \xi_o |\psi|^2 \\ \gamma = -s_p \xi \cos(3\theta_c) |\psi|^2 \\ \eta = -s_p \xi \sin(3\theta_c) |\psi|^2 \end{cases}, \quad (10)$$

which show that strain is higher in regions where the electron is localized. The sign in the first equation is plus for electrons and minus for holes. The other two equations change sign depending on the chirality of the nanotube via s_p . The lengths ξ_o , ξ read

$$\begin{cases} \xi_o = \frac{3\tau'}{4\sigma c (v_L^2 - v_T^2)} \\ \xi = \frac{3\tau(1+l/e)}{8\sigma c v_T^2} \end{cases} \quad (11)$$

and are inversely proportional to the circumference.

From (3) we have for the total elongation and torsion of the tube $\Delta L = \int (\gamma_o - \gamma) dz$ and $r\Delta\phi = \int \eta dz$, and thus from (10) and because of normalization of ψ , we obtain

$$\begin{cases} \Delta L = \pm \xi_o + s_p \xi \cos(3\theta_c) \\ r\Delta\phi = -s_p \xi \sin(3\theta_c) \end{cases} \quad (12)$$

where, *repetita juvant*, the sign in the first equation is plus for electrons and minus for holes. Note that the overall elongation and torsion of the tube due to electron/hole injection is independent of the actual shape of ψ . Unfortunately, that also implies that self-trapped electronic excitations cannot be recognized by global observations such as overall elongation, but solely via local mechanical features.

Equations (12) generalize to arbitrary chirality what already found by Nisoli *et al* for doping of zig-zag nanotubes [20]. The first result from (12) is that electron/hole injection induces no torsion for zig-zag nanotubes (which correspond to $m = 0$, thus $\theta_c = 0$), at least in our approximation that neglects curvature corrections. On the other hand, torsion would be maximum for tubes approaching the armchair configuration (the armchair themselves are metallic and thus excluded from this study): that would be $n = m + 1$. Again from (12) we obtain that elongation is always positive for electrons in nanotubes with $p = 2$, whereas is always negative for holes in nanotubes with $p = 1$. The maximum in both cases is achieved by zig-zag nanotubes ($\theta_c = 0$). These results are in agreement with the density functional study of Ref. [14], who found elongation for electrons in (11,0) zig-zag, and contraction for holes in (7,0) zig-zag.

Analysis of the general case requires knowledge of the quantities ξ_o , ξ . If $\xi > \xi_o$, the first equation of (12) tells us that chirality can change the sign of ΔL s_p and thus predicts shortening for self trapped electrons, yet elongation for holes, in certain tubes. This seems to be the

case, from a rough estimate: we use $e = 1.42 \text{ \AA}$ and the Harrison scaling for the hopping parameters [23], which are $\tau' = 2t'$, $\tau = 2t$, with $t \simeq 2.8 \text{ eV}$, $t' \simeq 0.68 \text{ eV}$ [24]. For the speeds of sound in graphene we use $v_T = 1.4 \cdot 10^4 \text{ m s}^{-1}$, $v_L = 2.16 \cdot 10^4 \text{ m s}^{-1}$ as in Mahan [16]; finally from the density of graphite 2.26 gm cm^{-3} and the interlayer distance at 3.4 \AA the surface density of graphene can be estimated $\sigma \simeq 7.6 \cdot 10^{-7} \text{ Kg m}^{-2}$. We obtain $\xi_o \simeq 2.5 \cdot 10^{-2} \text{ \AA}^2/2r$, $\xi \simeq 8.7 \cdot 10^{-2} \text{ \AA}^2/2r$. For a larger nanotube of 1 nm in diameter, 10^3 electrons can give a 1nm elongation. Since the elongation and torsion are inversely proportional to the radius of the nanotube: these effects become stronger for small radii, for which our treatment is only a first order approximation.

From (9) we find that the inner displacement

$$\begin{cases} q_\phi = 0 \\ q_z = -s_p \xi (l + l') |\psi|^2 \end{cases} \quad (13)$$

with $l' = 4v_T^2/\omega_T^2(e+l) \simeq 0.35 \text{ \AA}$ (computed from $v_T = 1.4 \cdot 10^4 \text{ ms}^{-1}$ and $\omega_T = 3 \cdot 10^{14} \text{ s}^{-1}$). Thus, the inner displacement is always parallel to the nanotube axis, while its absolute magnitude is independent of the chiral angle. On the other hand, its orientation depends on the chiral indices, thus suggesting that polarons can induce highly non monotonic anomalous bond contractions/expansion and thus hardening/softening of optical modes [8–10, 20].

Finally, by substituting the expression for the elastic fields (10, 13) into the last equation of (9), one finds a nonlinear Schrödinger equation for the envelope ψ

$$\epsilon_p \psi = -\frac{\hbar^2}{2m} (\partial_z^2 \psi + 4\chi |\psi|^2 \psi) \quad (14)$$

where the reciprocal length χ is found to be

$$\chi e = \frac{\pi}{4\sigma c^2 t} \left[\frac{\tau^2(e+l)(e+l+l')}{v_T^2 e^2} + \frac{\tau'^2}{4(\hat{\mu} + \hat{\lambda})} \right] \quad (15)$$

where we have used the expression $m = 2\pi\hbar^2/(9ect)$ for the effective mass of the electron obtained from the formula for the band gap [2]. The well known self-bound solution of (14)

$$\psi(z, t) = \sqrt{\frac{\chi}{2}} \cosh^{-1}(\chi z) e^{-i\epsilon_p t/\hbar} \quad (16)$$

corresponds to a polaron of energy $\epsilon_p = -\frac{\hbar^2 \chi^2}{2m}$ and length $a = \chi^{-1}$. Remarkably unlike the amplitude of the elastic deformations, *the length and thus the energy of the polaron does not depend on the chiral angle*. Also polaron length *is the same for electrons and holes*. This latter statement is in contrast with results reported by Verissimo-Alves [14]: while for the (11,0) nanotube they find about the same polaron length for electron (39 nm)

and hole (40 nm), for the (7,0) case the electron polaron has a length of 59 nm, while the hole is 21 nm long. The polaron length $a = \chi^{-1}$ can be estimated from (15) to be of several hundred angstroms for nanotubes of a few nanometers in diameter, in agreement with estimate based on DFT results [14].

Finally, for completeness, we calculate the radial variation of the nanotube $\Delta r/r = p^{\phi\phi}$. From (10) and (16) we see that the maximum radial variation corresponds to the maximum of ψ (at $z = 0$) or

$$\frac{\Delta r}{r} = \pm \frac{\xi_o}{2a} - s_p \frac{\xi}{2a} \cos(3\theta_c), \quad (17)$$

positive sign for electrons, negative for holes. There is always a radial shrinking in correspondence of self-trapped holes in nanotubes with $p = 2$, and radial expansion for electrons in nanotubes with $p = 1$, as partially confirmed by density functional findings of Ref. [14].

While the casuistic of excitons is too rich to be dealt with here [13], we can still offer a few considerations for the E_{11} case. As couplings of electron and holes with anisotropic deformations γ_o cancel each other, we must take $\nu' = 0$ and thus $\xi_o = 0$ in our equations. Hence, we can have optomechanical effects of both elongation or contraction, depending on the chiral indices, as predicted by (12) with $\xi_o = 0$.

The treatment above applies to static polarons in not too small nanotubes, as we neglect the breaking of honeycomb symmetry brought up by the chiral vector. That would introduce new terms in the elastic energy and result in curvature corrections for very small radii [20]. Also, for small radii, orbital hybridization imposes a more sophisticated tight binding treatment. For the propagating polaron, another symmetry breaking comes from the velocity vector, directed along the nanotube axis. Even for large nanotubes, we expect corrections (at lowest order quadratic) in the speed of the traveling polaron. [25].

In conclusion, we have calculated the elastic deformations and electronic structure of self-trapped electronic states in single wall carbon nanotubes. We found that elongation and torsion depend on the chiral angle whereas the polaron length does not. The inner displacement is always axial and changes orientation depending on the chiral indices: this suggests a chirality dependent bond lengthening/contraction and optical mode frequency shift. Extension of this model to excitons is particularly interesting.

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- [26] The expression for V_{el} is simplified in the long polaron approximation. Using the notation of Ref. [20], we can neglect terms in $\partial^i q^j$ (the dispersion in the optical branches) as long as $(\mu - \mu')/a^2, (\lambda - \lambda')/a^2 \ll \alpha$, where a is the length of the polaron. Since $(\mu - \mu'), (\lambda - \lambda')$ are the order of the square of the speed(s) of sound in graphene[20] or about $10^8 \text{ m}^2\text{s}^{-2}$, whereas α can be expressed in terms of the graphite-like optical frequency[20] $\alpha = \omega_T^2/4 \sim 10^{28} \text{ s}^{-2}$ and we have for the length of the polaron[14] $a \sim 10 \text{ nm}$, those ratios are thus of the order of 10^{-4} .