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Polaron-induced deformations in carbon nanotubes studied using the bicontinuum model

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We compute the 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 presented two field model for electromechanics of carbon nanostructures. We find that deformations are highly nonmonotonic in the chiral angle, whereas the length of the polaron is not. Applications include nanomechanical devices as electrically or optically driven nanoactuators.

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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 nanoactuators) or shifts in Raman phonon modes.[8–10] 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 found lengths of the order of 40–60 nm and energies of order of $10^{-2}-10^{-1}$ meV. Their long polaron approximation is confirmed by atomistic numerical analysis, e.g., of Bratek *et al.*[15]

Chiral indices are known to play dramatic role in the physics of carbon nanotubes. Not only they dictate the metallicity, they are known to control in a very delicate way electromechanical and vibrational effects.[8–10] It is of outmost importance both theoretically and technologically to be able to predict for which chirality a polaron induces, e.g., contraction rather than elongation, radial expansion rather than shrinking, or torsion etc. While Ref. 14 first suggested the presence of polarons, their simplified model cannot address the complex deformations in carbon nanotubes and completely ignores chirality dependence. On the other hand, more complete treatments based on atomistic models are too complex to be solved analytically or too computationally costly to return detailed answers for a general case.

In this Brief Report, we employ a recently presented[16] bicontinuum model to solve this predicament and calculate the full range of deformations induced by self-trapped electrons/holes for the general carbon nanotube. We find that deformations are, as one would expect, highly nonmonotonic in the chiral indices, even with abrupt change in signs in nanotubes of about the same chirality and about the same radius.

In a recent work, Nisoli *et al.*[16] 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 graphene 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[17] $u^{ij}=\partial^{(i}u^{j)}$, $v^{ij}=\partial^{(j}v^{i)}$, and wrote the elastic energy via considerations of symmetry. Unlike Ref. 16, 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 variables, the elastic energy of Ref. 16 becomes $W_{\mathrm{el}}=\int\sigma V_{\mathrm{el}}[p,q]\mathrm{d}x^2$, with

$$V_{\mathrm{el}}[p,q]=\hat{\mu}p^{ij}p_{ij}+\frac{\hat{\lambda}}{2}p^i_ip^j_j+\frac{1}{2}\omega_\Gamma^2q^2-2\beta e_{ijk}q^ip^{jk}, \qquad (1)$$

where we have employed the long polaron approximation to neglect the dispersion of the optical branches.[18] 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,

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

There are thus four parameters: ω_Γ, the graphitelike 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 $\ell\equiv4\beta/\omega_\Gamma^2=0.3$;[16] and the generalized Lamè symbols $\hat{\mu}$, $\hat{\lambda}$, which can be expressed in terms of the longitudinal and

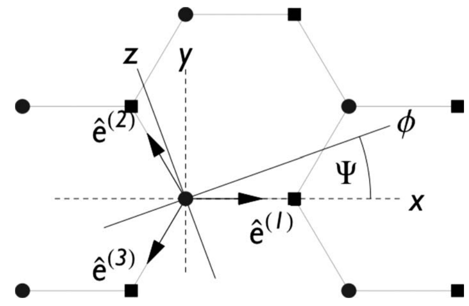

FIG. 1. The two sublattices (circles and squares) of graphene and the three unit vectors $\hat{e}^{(l)}$ used in the text. ϕ, z are cylindrical coordinates of a tube, while $\Psi=\pi/6-\theta_c$ with θ_c the chiral angle.

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

$$\begin{aligned} p^{\phi\phi} &= \gamma_o+\gamma, \\ p^{zz} &= \gamma_o-\gamma. \\ p^{\phi z} &= p^{z\phi}=\eta. \end{aligned} \tag{3}$$

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

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

(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. 16, 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 Eq. (1) via $p^{\phi\phi}=(\partial_\phi p^\phi+p^r)/r$.[17] 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 additional terms 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 semiconducting nanotube, they can be described in terms of an envelope wave-function ψ (Ref. 19) of energy density

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

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

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

(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 zone 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:[16] $\mathrm{d}t^{(l)}=-\tau\hat{e}_i^{(l)}\hat{e}_j^{(l)}p^{ij}+\tau\hat{e}_i^{(l)}q^i/e$ are the three nearest-neighbor hopping integrals along the three bonds of unit vectors $\hat{e}^{(l)}$, whereas $\mathrm{d}t'^{(l)}=-\tau'\hat{a}_i^{(l)}\hat{a}_j^{(l)}p^{ij}$ are the hopping integrals along the three directions $\hat{a}^{(l)}$ of the next-nearest neighbors. (τ, τ' are often called scaling parameters).[20] Following along the line of Refs. 5 and 16, one can calculate the variation in 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 Eq. (6) and in particular

$$\begin{aligned} \nu' &= \mp 3\tau', \\ \nu &= \frac{3}{2}s_p\tau. \end{aligned} \tag{7}$$

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 $p\equiv[(n-m)\mathrm{mod}\ 3]$. This difference in sign behavior between ν and ν' was previously recognized as causing indices dependence and nonmonotonicity in the doping-induced shift of Raman frequencies and anomalous bond contraction/expansion in zigzag nanotubes.[8–10,16] 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

$$\mathcal{H}=-\psi^\dagger\frac{\hbar^2\partial_z^2}{2m}\psi+\sigma cV_{\mathrm{el}}+E_{\mathrm{ep}} \tag{8}$$

where V_{el} is given by Eq. (4), E_{ep} is given by Eq. (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,

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

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

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

which show that strain is higher in regions where the electron is localized. We find $\xi_o=\frac{3\tau'}{4\sigma c(v_{\mathrm{L}}^2-v_{\mathrm{T}}^2)}$, $\xi=\frac{3\tau(1+l/e)}{8\sigma c v_{\mathrm{T}}^2}$ inversely proportional to the circumference. The sign in the first equation of (10) is plus for electrons and minus for holes. The other two equations change sign depending on the chirality of the nanotube via s_p.

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

$$\begin{aligned} \Delta L &= \pm \xi_o + s_p \xi \cos(3\theta_c) \\ r\Delta\phi &= - s_p \xi \sin(3\theta_c), \end{aligned} \tag{11}$$

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 has overall elongation, but solely via local mechanical features.

Equation (11) generalize to arbitrary chirality what already found by Nisoli *et al.*[16] for doping of zigzag nanotubes. The first result from Eq. (11) is that electron/hole injection induces no torsion for zigzag 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 Eq. (11) 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 zigzag 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) zigzag, and contraction for holes in (7,0) zigzag.

Analysis of the general case requires knowledge of the quantities ξ_o, ξ. If $\xi > \xi_o$, the first equation of Eq. (11) tells as that chirality can change the sign of ΔL 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 $e=1.42$ Å and the Harrison scaling for the hopping parameters,[20] which are $\tau' = 2t'$, $\tau = 2t$, with $t \simeq 2.8$ eV, $t' \simeq 0.68$ eV.[21] For the speeds of sound in graphene we use $v_\mathrm{T}=1.410^4$ m s^{-1}, $v_\mathrm{L}=2.1610^4$ 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 Å the surface density of graphene can be estimated $\sigma \simeq 7.610^{-7}$ Kg m^{-2}. We obtain $\xi_o \simeq 2.510^{-2}$ Å$^2/2r$, $\xi \simeq 8.710^{-2}$ Å$^2/2r$. For a larger nanotube of 1 nm in diameter, 10^3 electrons can give a 1 nm 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 Eq. (9) we find the inner displacement

$$\begin{aligned} q_\phi &= 0 \\ q_z &= - s_p \xi (l + l') |\psi|^2, \end{aligned} \tag{12}$$

with $l' = 4v_\mathrm{T}^2/\omega_\Gamma^2(e+l) \simeq 0.35$ Å (computed from $v_\mathrm{T} = 1.410^4$ ms^{-1} and $\omega_\Gamma = 310^{14}$ 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 nonmonotonic anomalous bond contractions/expansion and thus hardening/softening of optical modes.[8–10,16]

Finally, by substituting the expression for the elastic fields Eqs. (10) and (12) into the last equation of Eq. (9), one finds a nonlinear Schrödinger equation for the envelope ψ

$$\epsilon_p \psi = - \frac{\hbar^2}{2m} (\partial_z^2 \psi + 4\chi |\psi|^2 \psi) \tag{13}$$

in which the reciprocal length χ is found to be

$$\chi e = \frac{\pi}{4\sigma c^2 t} \left[\frac{\tau^2 (e+l)(e+l+l')}{v_\mathrm{T}^2 e^2} + \frac{\tau'^2}{4(\hat{\mu} + \hat{\lambda})} \right] \tag{14}$$

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 Eq. (13)

$$\psi(z,t) = \sqrt{\frac{\chi}{2}} \cosh^{-1}(\chi z) e^{-i\epsilon_p t/\hbar} \tag{15}$$

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. We suspect that the discrepancy originates from a sign error in the quantity which Ref. 14 defines as λ_z, as analysis of their Fig. 2 confirms. In our formalism and using the Harrison scaling and parameters above, we have for a zigzag nanotube $\lambda_z = -3s_p t/2 \mp 3t'$ and estimate $\lambda_z = -6.3$ eV for electrons, -2.2 eV for holes, for a (10,0) nanotube—in the ballpark with the Ref. 14 values of -8.3, -2.4 eV. Instead we find a sign mismatch for the (7,0) where our estimates are $+2.2$ eV for electrons, $+6.3$ eV for holes, whereas they have -1.6 eV, $+7.8$ eV. The polaron length $a = \chi^{-1}$ can be estimated from Eq. (14) to be of several hundred angstroms for nanotubes of a few nanometers in diameter, in agreement with estimate based on density functional theory results.[14]

Finally, for completeness, we calculate the radial variation in the nanotube $\Delta r/r = p^{\phi\phi}$. From Eqs. (10) and (15) we see that the maximum radial variation corresponds to the maximum of ψ (at $z=0$) or

$$\frac{\Delta r}{r} = \pm \frac{\xi_o}{2a} - s_p \frac{\xi}{2a} \cos(3\theta_c), \tag{16}$$

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 Eq. (11) 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 additional terms in the elastic energy in the form of curvature corrections for very small radii.[16] Also, for small radii, orbital hybridization imposes a more sophisticate 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 expects corrections (at lowest-order quadratic) in the speed of the traveling polaron.[22]

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 depends highly non monotonically on the wrapping indices, 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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[18] The expression for V_{el} is simplified in the long polaron approximation. Using the notation of Ref. 16, 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[16] or about $10^8\ \mathrm{m}^2\,\mathrm{s}^{-2}$, whereas α can be expressed in terms of the graphitelike optical frequency[16] $\alpha=\omega_\Gamma^2/4\sim10^{28}\ \mathrm{s}^{-2}$ and we have for the length of the polaron[14] $a\sim10$ nm, those ratios are thus of the order of 10^{-4}.

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