Electron-phonon coupling and Peierls transition in metallic carbon nanotubes

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We reexamine the putative Peierls transition in a (5,5) metallic nanotube. We show that the conduction electrons at the Fermi level do not couple to the longitudinal acoustic phonon but rather to a folded-in graphene zone edge phonon having the proper Kékulé modulation symmetry. The calculation for the mean-field transition temperature gives 15 K, a value comparable to previous estimates. We discuss the significance of this transition temperature.

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Since their discovery by Ijima in 1991, carbon nanotubes have attracted a lot of interest due to their unusual geometry and their structural and electronic properties. Band calculations have stressed the one-dimensional (1D) character of single-wall carbon nanotubes (SWCNT). They showed moreover that, depending on their diameter and helicity, a SWCNT can either be metallic or semiconducting. The metallic tubes provide an excellent environment for one-dimensional (1D) conductor physics. The existence of a putative Peierls transition due to the electron-phonon coupling has already been addressed by Mintmire and Huang who predicted the occurrence of a Peierls transition at 1K and 9K respectively. We propose to reexamine the Peierls transition owing to what we believe to be a wrong selection of soft phonon mode by Huang. The longitudinal polarization of the phonon they considered, taken from, cannot lead to a Kékulé instability natural to graphene, the two-dimensional (2D) carbon sheets that are rolled up to form the tubules. We will consider in the following the (5,5) armchair SWCNT which presents metallic properties. We shall reevaluate its phonon spectrum, deduce the electron-phonon coupling amplitude, and finally estimate the mean-field Peierls transition temperature.

We first recalculate the phonon spectrum of graphene by the dynamical matrix method using the force constants obtained by Maeder. We solve numerically the secular equation for the phonons. The polarization vector of the phonons is written as

$$\mathbf{e} (q, \nu) = (\mathbf{e}_A (q, \nu), \mathbf{e}_B (q, \nu)),$$

where $\mathbf{e}_r (q, \nu)$ is the polarization of one of the two atoms $r = A, B$ in the unit cell for the phonon of wave vector $q$ and branch $\nu$. Here $\mathbf{e}_r$ has two components along the mutually orthogonal directions $z$ and $y$ (the tube axis direction) in the sheet respectively (see Fig. 1). These polarizations satisfy the relation $\mathbf{e} (-q, \nu) = \mathbf{e} (q, \nu)^*$. There are two phonon groups relevant to our study. The first one is at the $K$ points in the 2D hexagonal first Brillouin zone (BZ) of graphene (see Fig. 1). Its phonons have the wave vector $q = (0, \pm 4\pi/3a)$ or $(\pm 2\pi/\sqrt{3}a, \pm 2\pi/3a)$. The polarizations for $q = (0, 4\pi/3a)$ are given by

$$\mathbf{e} (q, 1) = \frac{1}{2} (1, i, 1, 1), \mathbf{e} (q, 2) = \frac{1}{2} (-i, -1, i, 1),$$

$$\mathbf{e} (q, 3) = \frac{1}{2} (i, -1, -i, 1), \mathbf{e} (q, 4) = \frac{1}{2} (i, -1, i, 1)$$

(2)

The second group, to which the acoustic phonon with longitudinal polarization belongs, has polarizations

$$\mathbf{e} (q, 1) = \frac{1}{\sqrt{2}} (0, 1, 0, -1), \mathbf{e} (q, 2) = \frac{1}{\sqrt{2}} (-i, 0, i, 0),$$

$$\mathbf{e} (q, 3) = \frac{1}{\sqrt{2}} (0, 1, 0, 1), \mathbf{e} (q, 4) = \frac{1}{\sqrt{2}} (i, 0, i, 0)$$

(3)

for $q = (0, -2\pi/3a)$. Here $a/\sqrt{3}$ is the carbon-carbon distance in graphene.

The nanotube is constructed by rolling the sheet of graphene in the prescribed fashion. The (5,5) SWCNT has the right diameter to be capped at the ends by half a $C_{60}$ sphere. Its unit cell has length $a$ and contains 20 atoms (see Fig. 1). The requirement of periodicity around the nanotube imposes the following quantization condition on $q_m$,

$$q_m = (2\pi/5\sqrt{3}a) m, \quad -5 < m < 5$$

is an integer. The equilibrium position of an atom on the nanotube is specified by $(n, s)$, $n$ indicating the position $R_n$ of the unit cell along the nanotube axis and $s$ referring to the position $d_s$ of the atom within the unit cell, so that

$$R_{n,s} = R_n \hat{y} + d_s.$$  

(4)

Because of the difference in the length of the unit cell of SWCNT (5,5) with the one of graphene, the first Brillouin zone has a smaller length in the $\hat{y}$ direction given by...
2π/a. We can than approximate the phonon spectrum of the nanotube by folding the spectrum of graphene, subject to the quantization rule for q, to above, into the BZ of the nanotube. We can now write the polarization vector $S_1(q, ν, m)$ of atom $s$ for the phonon of wave number $q$ (along the axis of the tube) corresponding to branch $ν$ and quantum number $m$ in terms of those in graphene:

$$S_1(q, ν, m) = \frac{1}{\sqrt{10}} e^{i(ν+G_q)\frac{q}{2} + iq_s \frac{q}{2}} e_{A(q)}(\sqrt{q}, ν),$$

$$S_3(q, ν, m) = \frac{1}{\sqrt{10}} e^{i(ν+G_q)\frac{q}{2} + iq_s \frac{q}{2}} e_{A(q)}(\sqrt{q}, ν), \quad (5)$$

where $q_y = q + G_q$ for $|q| ≤ π/a$, and $G_q = n_q(2π/a)$ is a reciprocal lattice wave number of the nanotube. Also, one has the property $S_{s+4} = \exp(ik_s\sqrt{3a}) S_s$. The result of this folding-in for the branches of interest here is shown in Fig. 2.

The electron-phonon interaction Hamiltonian, treated within the tight-binding approximation, is written as

$$H_{e-ph} = \frac{1}{L} \sum_{ν,m,p,p',k,k'} g_{ν,m}^{k,k',p'}(G)C_{k,p,σ}^{+}C_{k',p',σ} \times (b_{q,ν,m} + b_{q,ν,m}^{+}), \quad (6)$$

where $L$ is the length of the tube, $C_{k,p,σ}^{+} (C_{k,p,σ})$ is the creation (annihilation) operator for an electron with wave vector $k$ and spin $σ$ in band $p$, $G$ is a reciprocal lattice wave number such that $q = k - k' - G$ is within the nanotube’s first BZ, and $b_{q,ν,m}$ is the phonon operator. The electron-phonon interaction matrix element $g_{ν,m}^{k,k',p'}(G)$, is given within the tight-binding approximation by the following expression:

$$g_{ν,m}^{k,k',p'}(G) = \left(- \frac{\hbar ω_{ν,m - k,k' - G}}{2π} \right)^2 \sum_{α,α',s,s'} \{ e^{-ikR_{αs}}[S_{α}(k - k' - G, ν, m)]_{αs'} - e^{-ikR_{α's'}}[S_{α'}(k - k' - G, ν, m)]_{αs} \}, \quad (7)$$

where $μ$ is the mass per unit length of the tube, $ω_{ν,m}$ is the phonon frequency, $J(n, s; n', s')$ is the matrix element of the atomic potential connecting orbitals on nearest-neighbor atoms $(n, s)$ and $(n', s')$, and $U(k)$ is the Bloch eigenvector that diagonalizes the purely electronic part of Hamiltonian. The elements of $U(k)$ obey to the periodic boundary condition $U_{1,p}(k) = U_{21,p}(k)$ and correspond to the graphene Bloch eigenvectors folded into the nanotube’s BZ. The Fermi level is situated at $k_F = (2π/3a)$ at the crossing of two bands having the dispersion relations $ε_p(k) = ±J_0[1 - 2 \cos(ka/2)]$ with $p = 1, 2$. The band crossing corresponds to the $K$ point of the BZ of graphene of Fig. 1b. The wave functions at the six $K$ points bear the signature of the Kékulé bond arrangement of graphene which can be obtained by coupling to the $\mathcal{G} = (0, ±4π/3a), (±2π/3a, ±2π/3a)$ phonons. It is now possible to calculate the electron-phonon coupling amplitudes for these two conduction bands by using the eigenvectors $U(k)$ given in the article of Jishi.

It is important to realize at this point that the momentum conservation condition $q = k - k' - G$ imposes that $G ≠ 0$ whenever $|k| = |k'| = k_F$ since $|k - k'| = 4π/3a$ is outside the first BZ of the nanotube and must be brought back within by $aG = 2π/a$. As a consequence of this, one has $|q| = 2π/3a$. There are two possibilities of interest here. The first corresponds to a graphene phonon having $|q| = |q + G_q| = 4π/3a$ for $m = 0$ or $|q| = |q| = 2π/3a$ for $m = 0$. These are the $K$ point phonons of graphene. The other is $|q| = |q| = 2π/3a$ for $m = 0$ to which the acoustic phonon with longitudinal polarization used by Huang and Jishi belongs (see Fig. 2).

![Phonon dispersion of the (5,5) nanotube](image_url)

**FIG. 2.** Phonon dispersion of the (5,5) nanotube coming from the folded-in $q' = (0, q_0)$ and the $\mathcal{G} = (2π/3a, q_0)$ phonons of graphene which coalesce at $q = 2π/3a$. The circle contains the mode that couples the electrons at the Fermi level. The square shows the longitudinal mode previously used by other authors.

It should be apparent by now that the $K$ point phonons naturally couple to the Kékulé structure whereas the acoustic phonons, having strictly longitudinal polarization, cannot couple to the transverse (around the nanotube) part of the Kékulé modulation. Indeed, the circular polarization (order parameter) associated with the $|q| = |q + G_q| = 4π/3a$ and $m = 0$ phonon, as can be deduced from the polarizations above, corresponds to a Kékulé modulation. To show this, let us assume a non-zero order parameter $b_{K,M}^{i=0}$ giving rise to a displacement $u_{n,s} = \sqrt{\hbar \omega_{k_F,1,0}/2} S_s(-k_F, 1, 0) \exp[-i(k_F R_{n} - φ)] b_{K,M}$ and $c.c.$ One obtains the following relative displacements $d_{n,s,n',s'} = u_{n,s} - u_{n',s'}$:

$$d_{n,3,3} = -D \cos(π/3), \quad d_{n,2,3} = D \cos(π/3), \quad d_{n,1,2} = -D \cos(π/3), \quad d_{n+1,3,2} = D \cos(π/3), \quad (8)$$
where \( D = 2\sqrt{R\omega_{-kF,1}a/20} \) \( b_{KM} \), and \( \alpha(n) = (n-1)\pi/3 + \pi/2 - \phi \). This is the Kékulé modulation with period \( \Delta n = 3 \) or wavelength \( \Delta y = 3a \). The relative displacements lie along the carbon-carbon bond directions leading to maximum modulation of the electron hopping amplitude \( J_0 \) and thus maximum electron-phonon coupling.

In the situation were \( k (k') \) is near \(+kF (-kF)\) is, for the \( K \) point phonons having \( m = 0, 5 \), one finds

\[
g_{v,m}^{k,k',a}(2\pi/a) = g_{k,2;k',a}(2\pi/a) = 0 \quad \forall \nu = 1, \ldots, 4
\]  

for \( p \neq p' \) and

\[
g_{v,0}^{k,k',a}(2\pi/a) = g_{v,0}^{k,k',a}(2\pi/a) = 0, \\
g_{v,0}^{k,k',a}(2\pi/a) = (-1)^{p+1} \frac{4\pi \Omega}{a} \sin \left( \frac{k-k'}{4} a - \frac{\pi}{6} \right) \\
\times \cos \left( \frac{k+k'}{4} a - \frac{1}{2} \right), \\
g_{v,0}^{k,k',a}(2\pi/a) = (-1)^{p+1} \frac{4\pi \Omega}{a} \sin \left( \frac{k-k'}{4} a + \frac{\pi}{6} \right) \\
\times \cos \left( \frac{k+k'}{4} a + \frac{1}{2} \right) .
\]

for \( p = p' = 1, 2 \). Here \( \eta_p = q_0 J_0 \sqrt{\hbar a/2m\omega_0} \) \( (\omega_0 = \omega_{1+2a/3a,v,0}) \), where \( m_c \) is the mass of a carbon atom, and \( J(\bar{r}) \) is assumed to depend only on distance such that \( q_0 J_0 = [\partial J(\bar{r})/\partial |\bar{r}|]_{\bar{r}=0} \). It can be seen that \( g_{v,0}^{k,k',a}(2\pi/a) = 0 \) and \( g_{v,0}^{k,k',a}(2\pi/a) = -6i\eta_1/\sqrt{40} \) at \( k = -k' = kF \).

Furthermore it can be demonstrated that

\[
g_{v,0}^{k,1,k',1}(2\pi/a) = g_{v,0}^{k,2;k',2}(2\pi/a) = 0 \quad \forall \nu = 1, \ldots, 4.
\]

for all \( m = 0 \) and \( |q| = 2\pi/3a \) phonons (this includes the acoustic phonon). This result is different from the estimate of the other mentioned authors. We recover their result when evaluating \( g_{v,0}^{k,1,k',1}(0) \) or, equivalently, assuming the longitudinal polarization corresponds to a \( K \) edge phonons. This is probably at the origin of the confusion.

One can now estimate the mean-field transition temperature. After integrating the phonons in the interaction representation, the partition function of the system can be expressed as

\[
Z = Z_{ph} \text{Tr} \left\{ e^{-\beta H_{0,s} \varepsilon_{\phi}(k)} (\tau e^{\frac{\Delta H_{1}(\tau-\tau')d(\tau-\tau')}) \right\}
\]

where \( H_{0,s} = \sum_{p,k,\sigma} \varepsilon_p(k) C_{p,k,\sigma}^+ C_{p,k,\sigma} \), and \( H_{1}(\tau-\tau') \) is the retarded electron-electron interaction given by

\[
H_{1}(\tau-\tau') = \frac{1}{L} \sum_{p,k,\sigma} \sum_{p',k',\sigma'} D_{0}(q) \tau - \tau')
\]

This last expression can be alternatively written as

\[
H_{1}(\tau-\tau') = \sum_{p,k,\sigma,p',k',\sigma'} g_{v,0}^{k,p,k',p'}(2\pi/a) \left[ g_{v,0}^{k,p,k',p'}(2\pi/a) \right]^{*} \\
\times C_{k,p,\sigma}^{+} C_{k-q,\frac{1}{a}k+\frac{1}{a},p',\sigma}^{+} C_{k',q,\frac{1}{a}k'+\frac{1}{a},p',\sigma'}^{+} (13)
\]

and the Matsubara time Fourier transform of the phonon propagator is \( D_{0}(q,\omega_{m}) = -2\omega_{m,1,0}^{0}/(\omega_{m,1,0}^{0} + \omega_{m,2}^{2}) \). The order parameter associated with \( O_{KM} \), the operator that is naturally selected by the electron-phonon coupling, is the electronic density Kékulé modulation operator. To verify this, let us calculate the electron density \( (\Psi^*(\bar{r})\Psi(\bar{r})) \) where \( \Psi(\bar{r}) = \sum_{k,p,\sigma,n,s} e^{ik\bar{r}} U_{n,p}(k) \phi(\bar{r} - \bar{R}_{n,s}) C_{k,p,\sigma}, \phi(\bar{r} - \bar{R}_{n,s}) \) is the orbital of the carbon atom at \( \bar{R}_{n,s} \), and the average is taken over a broken symmetry situation having \( < O_{KM} > = \frac{1}{L} \sum_{\sigma} \left( C_{kF,1,1}^{+} C_{kF,1,1}^{+} C_{kF,2,2}^{+} C_{kF,2,2}^{+} - C_{kF,1,1}^{+} C_{kF,1,1}^{+} C_{kF,2,2}^{+} C_{kF,2,2}^{+} \right) \) \( \rho_{KM} e^{i\phi} \). One can show that

\[
(\Psi^*(\bar{r})\Psi(\bar{r})) = \frac{1}{2} \sum_{n,s \neq n',s'} \kappa(n, s; n', s') (14)
\]

in which only the bond densities contribute \( (n, s \neq n', s') \).

One has \( \kappa(n, 3; n, 4) = \frac{10}{9} \cos(2n\pi/3 - \phi) \), \( \kappa(n, 2; n, 3) = \frac{10}{9} \cos(2n\pi/3 - \phi) \), \( \kappa(n, 1; n, 2) = \frac{10}{9} \cos((n+1)/2\pi/3 - \phi) \), \( \kappa(n, 2; n, 1) = \frac{10}{9} \cos((n+1)/2\pi/3 - \phi) \), and \( \kappa(n, 2; n, 1) = \frac{10}{9} \cos((n+1)/2\pi/3 - \phi) \), Comparing these bond density modulations to the relative phonon displacements calculated earlier, one sees that the two coincide when putting \( \phi = \pi/2 - 2\pi/3 \).

We can now calculate the static Kékulé modulation susceptibility for the system at \( q = 2\pi/3a \). The random-phase approximation (RPA) result is given by

\[
\chi_{KM} = \frac{\chi}{1 - g(\omega_{M} = 0)(\chi_{0}^{0} + \chi_{0}^{1}) \chi_{0}^{0}}
\]

where \( \chi_{0}^{0} (\chi_{0}^{1}) \) is the bare RPA charge response function of the first (second) band \( \chi_{KM} = \chi_{1} + \chi_{2} \), and \( \chi = \chi_{0}^{0} + \chi_{0}^{1} - 2g(0)\chi_{0}^{0} \chi_{0}^{1} \). As \( g(0) \) and \( \chi_{0}^{0} + \chi_{0}^{1} \) are both negative, the susceptibility can diverge when the denominator goes to zero. This corresponds to a mean-field critical temperature given by

\[
\chi_{KM} = \frac{\chi}{1 - g(\omega_{M} = 0)(\chi_{0}^{0} + \chi_{0}^{1}) \chi_{0}^{0}}
\]
where 

$$T_c = 3.86 \ J_0 \exp \left( \frac{1}{2N(\varepsilon_F) g(0)} \right). \quad (19)$$

To obtain this pre-exponential constant, we did a numerical calculation of \(\chi_{10}(\chi_{20})\) using the exact dispersion given above and fitted it to a standard \(C \ln(D/T)\) form. Here, one has \(N(\varepsilon_F) = 2/\pi \sqrt{3aJ_0}\) and \(g(0) = -\frac{9}{10} \left( q_0^2 J_0^2 a \right) / \left( m_c \omega_0^2 \right)\). For a numerical estimate of \(T_c\), we take \(5a = 2.46 \ \text{Å}, J_0 = 2.2 \text{eV}, q_0 = 2.5 \text{Å}^{-1}\), along with our value of \(\hbar\omega_0 = 0.166 \text{eV}\) corresponding to the graphene \(K\) point phonon. We obtain \(T_c = 15.2 \text{K}\). This estimated Peierls temperature is of the same order as Huang’s even though the selected phonon mode is different. The reason is that although the numerical factor for our effective electron-phonon coupling amplitude is larger, our phonon frequency is also larger. The two effects nearly cancel each other.

Even though nothing much has changed for the numerical estimate of the Peierls-Kékulé mean-field transition, we feel it is important that people use the correct electron-phonon interaction coupling to the right phonon. This is important in conductivity or superconductivity calculations.

The predicted \(T_C\) would of course change if one were to take into account the modification in stiffness constants due to the curvature of the SWCNT. These changes would be quantitative, not qualitative. One may of course, because of the Mermin-Wagner theorem, question the validity of a mean-field transition in 1D systems. There is of course no transition. The mean-field \(T_C\) signals the occurrence of a pseudo-gap. Moreover, the mean-field formula is for adiabatic phonons. This is surely not the case here as the thermal energy at the putative transition \(k_B T_C\) is much smaller that the phonon energy. Quantum fluctuation effects would be considerable. They would wipe out the pseudo-gap.

The above analysis also presumes of an infinitely long nanotube. These are of course of finite (micron scale) length. The analysis would prevail as long as the coherence distance is smaller than the tube’s length.

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