Twist instability in strongly correlated carbon nanotubes

Wei Chen and A. V. Andreev
Department of Physics, University of Washington, Seattle, Washington 98195-1560, USA

A. M. Tsvelik
Department of Condensed Matter Physics and Materials Science, Brookhaven National Laboratory, Upton, NY 11973-5000, USA

Dror Orgad
Racah Institute of Physics, The Hebrew University, Jerusalem 91904, Israel

(Dated: July 14, 2008)

We show that strong Luttinger correlations of the electron liquid in armchair carbon nanotubes lead to a significant enhancement of the onset temperature of the putative twist Peierls instability. The instability results in a spontaneous uniform twist deformation of the lattice at low temperatures, and a gapped ground state. Depending on values of the coupling constants the umklapp electron scattering processes can assist or compete with the twist instability. In case of the competition the umklapp processes win in wide tubes. In narrow tubes the outcome of the competition depends on the relative strength of the e-e and e-ph backscattering. Our estimates show that the twist instability may be realized in free standing \((5, 5)\) tubes.

PACS numbers: 68.60.Bs, 71.10.Pm, 73.22.Gk

The band structure of armchair carbon nanotubes is metallic [1]. However, due to the Peierls mechanism the metallic state may become unstable at low temperatures. For undoped armchair tubes the possible instability modes are a lattice deformation with a finite wave vector [2] and the twist instability at zero wave vector [3, 4]. Previous studies of this instability were carried out either in the noninteracting electron approximation [2, 3, 4, 5, 6], yielding a very low instability temperature \(T \lesssim 0.1K\) even for the thin \((5, 5)\) nanotubes, or using \textit{ab initio} calculations in the local density approximation [7]. These treatments can not account for the Luttinger liquid effects, which are expected to be pronounced in these systems [8, 9].

Here we study the possibility of the Peierls instability in armchair carbon nanotubes in the presence of electron-electron (e-e) interactions. We find that in the absence of backscattering processes the Luttinger liquid correlation of electrons significantly enhance the onset temperature for the \textit{twist} Peierls instability. The enhanced transition temperature in narrow tubes can be easily reached experimentally. We show that depending on the values of the e-e umklapp coupling constants the umklapp processes [8, 9, 10, 11] either enhance or compete with the twist instability. The energy gap due to the umklapp processes increases slower with decreasing tube radius \(R\) than the gap due to the Peierls instability. In case of the competition the twist instability can occur only in narrow tubes. Based on the theoretical values [12, 13] of the electron-phonon couplings we estimate the Peierls gap in \((5, 5)\) tubes with \(R \sim 0.35\) nm to be of the order of \(70\) K. The gaps due to the umklapp processes are much harder to evaluate theoretically because of their strong sensitivity to the short range part of the Coulomb repulsion potential [10, 11]. Gate voltage scans of conductance for armchair tubes [14, 15] indicate that the umklapp gaps for \((5, 5)\) tubes are of order or below our estimates for the twist gap. This suggests that the Peierls instability may be realized in torsional nanomechanical resonators [17] based on \((5, 5)\) armchair tubes.

We consider an undoped free standing \((N, N)\) armchair carbon nanotube, see Fig. 1 (a). It is symmetric with respect to reflection in the plane that goes through the tube axis and maps the A and B sublattices onto each other. Thus both electron and phonon modes are characterized by parity, \(\pm 1\) [3]. The low energy electron spectrum is formed by two bands with opposite parity and zero angular momentum along the tube axis. These bands intersect at the two Dirac points as shown in Fig. 1 (b). Only the phonon modes with zero angular momentum along the tube axis couple to the low energy electron modes. Furthermore, only the backscattering part of the electron-phonon (e-ph) coupling can lead to the Peierls instability and is strongly enhanced by the Luttinger liquid correlations. We therefore neglect the forward scattering part of the e-ph coupling [26]. The backscattering by positive parity phonons involves large momentum transfer and corresponds to phonons with rather high frequencies, \(\sim 1000K\). This cuts off Luttinger liquid renormalization and results only in a finite softening of these phonons [18]. The Peierls instability arises from the coupling to the negative parity phonons with small momentum. There are three such phonon modes: transverse acoustic (TA) and longitudinal/radial optical (LO/RO) [3, 13]. The e-ph coupling arises from the
change in the hopping matrix element due to the atomic displacements. The coupling to the RO mode is due to the curvature of the tube and is smaller than the coupling to the LO and TA modes in $1/N$ [13]. We neglect it below. Its inclusion would only enhance the twist instability.

The phonon Hamiltonian can be written as

$$H_{ph} = \frac{\rho}{2} \sum_{q} \sum_{a=L,T} \left( |\hat{u}_a(q)|^2 + \omega_a(q)^2 |u_a(q)|^2 \right).$$

Here $\rho$ is the mass per unit length of the tube and $u_a(q)$ are Fourier components of atomic displacements. The index $a = L$ corresponds to the LO mode with momentum independent frequency $\omega_L(q) = \omega_L$ and $a = T$ corresponds to the TA mode with frequency $\omega_T(q) = s_T q$, $s_T$ being the speed of sound.

The free electron Hamiltonian can be written as

$$H_{0e} = -i\hbar v_F \sum_{\alpha \sigma} \int dx \psi_{\alpha \sigma}^+ (x) \partial_x \psi_{\alpha \sigma} (x).$$

Here $v_F \approx 8 \times 10^5 \text{ m/s}$ is the Fermi velocity, $\alpha = \pm 1$ is the valley index, $r = \pm 1$ represents right and left movers, and $\sigma$ is the electron spin.

The forward scattering part of the e-e interaction is much stronger than the backscattering part, the latter being small in $1/N$ [19]. The former can be written as

$$H_{\rho} = g_0 \int dx n^2 (x), \quad n(x) = \sum_{\alpha \sigma} \psi_{\alpha \sigma}^+ (x) \psi_{\alpha \sigma} (x).$$

Here we assumed that the Coulomb interaction is screened by e.g. a gate at a distance $d$, and the coupling constant being $g_0 \approx 2e^2 \ln(d/R)$.

The above electron Hamiltonian is bosonized by the standard procedure (see, for example, [20] [21])

$$\psi_{\alpha \sigma} (x) = \frac{F_{\alpha \sigma}}{\sqrt{2\pi \xi}} \exp\{-i\sqrt{\pi}[\Theta_{\alpha \sigma} (x) - r \Phi_{\alpha \sigma} (x)]\}. \quad (4)$$

Here $F_{\alpha \sigma}$ are the Klein factors, $\xi$ is a short distance of order of the radius of the nanotube, and $\Phi$ and $\Theta$ are boson fields satisfying the commutation relation

$$[\Phi_{\alpha \sigma} (x), \Theta_{\alpha' \sigma'} (x')] = -i\delta_{\alpha \alpha'} \delta_{\sigma \sigma'} \delta(x - x'), \quad (5)$$

with $\delta(x-x')$ being the step function. Introducing charge and spin modes combining different valleys,

$$\Phi_{\alpha \sigma} = [\Phi_{e++} + \alpha \Phi_{e-} + \sigma \Phi_{s+} + \alpha \sigma \Phi_{s-}] / 2,$n

$$\Theta_{\alpha \sigma} = [\Theta_{e++} + \alpha \Theta_{e-} + \sigma \Theta_{s+} + \alpha \sigma \Theta_{s-}] / 2,$$

we rewrite the forward scattering part of the electron Hamiltonian as

$$H_{0e} + H_{\rho} = \sum_j \frac{\hbar u_j}{2} \int dx [K_j^{-1} (\nabla \Phi_j)^2 + K_j (\nabla \Theta_j)^2].$$

Here $j = c\pm, s\pm$, $u_j = v_F / K_j$ with $K_j$ being the Luttinger parameter is the velocity of the $j$-th mode. For the three modes $j = c-, s\pm$, $K_j = 1$. For the charge mode $K_{c+} = 1 / \sqrt{1 + g_0^2 / \pi v_F \hbar}$. Below we will use the high charge stiffness approximation, $K_{c+} \ll 1$.

The coupling of electrons to the TA and LO phonons is described by the Hamiltonian

$$H_{ep} = \int dx M(x) [g_T \nabla u_T (x) + g_L u_L (x)], \quad (7)$$

with $M(x) = -i \sum_{\alpha r \sigma} \alpha r \psi_{\alpha r \sigma}^+ (x) \psi_{\alpha -r \sigma}$. The bosonized form of the operator $M$ is

$$M = -\frac{4}{\pi \xi} \left[ \prod_{\nu = \pm} \cos(\sqrt{\pi} \Phi_{c\nu}) \sin(\sqrt{\pi} \Phi_{sv}) \right. \left. + \prod_{\nu = \pm} \sin(\sqrt{\pi} \Phi_{c\nu}) \cos(\sqrt{\pi} \Phi_{sv}) \right]. \quad (8)$$

By writing $M$ in this form we adopted the convention $F_{\alpha r \sigma} F_{\alpha' r' \sigma'} = 1$. For $K_{c+} \ll 1$ the e-ph coupling leads to a strong renormalization of the phonon mode.

To the second order in the e-ph coupling the phonon propagator matrix becomes $D_{\omega_n, q} = [D_{0}^{-1} (\omega_n, q) + \Sigma (\omega_n, q)]^{-1}$, where $\omega_n = 2n\pi T$ is the Matsubara frequency, $D_{0}^{-1} (\omega_n, q) = \delta_{\alpha \alpha'} \delta_0 (\omega_n + \omega_n (q))$ is the bare phonon propagator, and $\Sigma (\omega_n, q)$ is the self energy due to the e-ph interaction. The latter has the form

$$\Sigma (\omega_n, q) = -P(\omega_n, q) \left( \frac{g_T^2 q^2 - ig_T g_L q}{g_L^2 q^2} \right). \quad (9)$$

where $P(\omega_n, q) = \int d\omega \omega \tau - i q \langle M(0) M(\omega)\rangle$ and $\langle \ldots \rangle$ denotes thermal averaging with respect to the forward scattering Hamiltonian [4]. In the bosonized representation it is given by

$$P(\omega_n, q) = \int 2d^2 r \frac{e^{i\omega_n \tau - i q \cdot \xi}}{(\pi \xi)^2} \sum_j \langle (\Phi_j (r) - \Phi_j (0))^2 \rangle.$$
In the long wavelength limit, \( q, \omega \to 0 \) and for \( K_{c+} \ll 1 \) we obtain,
\[
P(0,0) = P = \frac{1}{v_F} \left( \frac{\beta v_F}{\pi \xi} \right)^\frac{1}{2} \frac{1}{\pi^2} B^2 (3/8, 1/4),
\]
where \( B(a, b) \) is the Euler Beta function.

The renormalized phonon frequencies are given by the poles of \( \det(D(\omega_n, q)) \) analytically continued to real frequencies. The instability first appears when the renormalized frequency of the acoustic mode, \( \omega_T \) turns to zero,
\[
\omega_T^2 \equiv \frac{1}{\pi^2} \frac{1}{1 - \frac{\tilde{g}_T^2 + \tilde{g}_L^2}{v_F^2} P} = 0,
\]
where \( \tilde{g}_T = g_T / \sqrt{\rho s_2 v_F} \) and \( \tilde{g}_L = g_L / \sqrt{\rho o_2 v_F} \) are the characteristic dimensionless e-ph coupling constants for TA and LO phonons respectively. The mean field twist instability temperature is then
\[
T_c = \left( \frac{\tilde{g}_T^2 + \tilde{g}_L^2}{\pi \xi} \right) \frac{v_F}{2} B^2 \left( \frac{3}{8}, \frac{1}{4} \right).
\]

In one dimension fluctuations shift mean field instabilities to zero temperature. In the given case the order parameter \( \nabla u \) is real and the instability is of the Ising type. As is the case for the Ising model, a finite order parameter exists only at \( T = 0 \) whereas at finite \( T \) we have a state with a finite density of solitons (domain walls separating areas with different sign of \( \nabla u \)). The mean field \( T_c \) is, however, not devoid of meaning and gives an estimate of the spectral gaps associated with the strong electron-phonon coupling. The exact composition of the excitation spectrum is currently unknown. Using the Feynmann’s variational principle we can estimate the magnitudes of the gaps of the singlet excitations of fields \( \Phi_j \) [20]. These excitations represent small fluctuations around the minima of the action. In addition to them there are kinks of these fields. More complete analysis of the spectrum will be given in the extended version of this paper. For the condensed state, we assume the lattice has a static deformation, \( \nabla u_T = \eta, u_L = \xi \), and for the electronic degrees of freedom we use a variational action of the form,
\[
S_0 = \frac{1}{2} \sum_j \int \frac{dxdr}{K_{u_j}} \left[ \Phi_j^2 + \frac{v}{\xi} (\nabla \Phi)^2 + \Delta_j^2 \Phi_j^2 \right],
\]
in the \( K_{c+} \to 0 \) limit,
\[
\eta = \frac{1}{\pi^2} \frac{g_T}{\rho s_2 v_F} \prod_{j \neq c+} \left( \frac{\Delta_j}{v_F} \right)^\frac{1}{2},
\]
\[
\xi = \frac{1}{\pi^2} \frac{g_L}{\rho o_2 v_F} \prod_{j \neq c+} \left( \frac{\Delta_j}{v_F} \right)^\frac{1}{2},
\]
\[
\frac{\Delta_j^2}{2K_{u_j} u_j} = \frac{1}{\xi} (g_T \eta + g_L \xi) \prod_{j \neq c+} \left( \frac{\Delta_j}{v_F} \right)^\frac{1}{2}.
\]
This gives identical gaps for the four electron modes,
\[
\Delta_j = \frac{v_F}{\xi} \left( \frac{8(\tilde{g}_T^2 + \tilde{g}_L^2)}{\pi} \right)^2,
\]
and the spontaneous twist angle
\[
\eta = \frac{\tilde{g}_T}{\sqrt{\frac{\pi}{2 \xi}} (\tilde{g}_T^2 + \tilde{g}_L^2)} \frac{\Delta}{\sqrt{\rho s_2 v_F}}.
\]

In the framework of the tight binding model, the values of the coupling constants can be expressed [12, 13, 22, 23] in terms of the derivative, \( \frac{\partial J(r)}{\partial r} \) of the transfer integral \( J(r) \) with respect to the bond length \( r \). For armchair nanotubes, these coupling constants were obtained to be: \( g_T = 3 \frac{\partial J(r)}{\partial r} \) and \( g_L = 3 \frac{\partial J(r)}{\partial r} \), where \( a = 2.5 \) Å is the graphene lattice constant and \( \frac{\partial J(r)}{\partial r} = -\lambda J_0 / c \) with \( J_0 = 2.6 \) eV the hopping integral, and \( c = 1.4 \) Å the bond length [23]. Here \( \lambda \) is a dimensionless constant, whose theoretical value is 2 [14]. The linear mass density for an \((N, N)\) armchair nanotube is \( \rho = 4NM/a \) with \( M \) being the carbon atom mass. The twiston phonon velocity \( s_T \approx 1.4 \times 10^4 m/s \) and the LO phonon energy \( \omega_T \approx 0.18 \) eV [3]. Thus both \( \tilde{g}_T \) and \( \tilde{g}_L \) are proportional to \( 1/\sqrt{R} \). For a \((5, 5)\) armchair nanotube with \( R \approx 0.35 \) nm, the transition temperature from Eq. (12) is about \( 40 \) K and the gap from Eq. (17) is about \( 70 \) K. As expected, the mean field instability temperature and the gap have the same order of magnitude. The twist angle is \( \eta \approx 3 \times 10^{-4} \).

As mentioned above the soliton effects will restore the symmetry at finite temperatures. However, if the length of the tube is shorter than the typical intersoliton distance, at experimental time scales the system will appear twisted in one direction. The estimated characteristic twist angle for \((5, 5)\) nanotubes, \( \sim 0.01^\circ \), is too small to be detected by STM imaging. However, for a freely suspended tube clamped at one end the accumulated rotation angle at a distance \( x \) from the clamp, \( \theta(x) = \eta x / R \), becomes substantial for \( x \sim 1 \) \( \mu \)m. This twist can be detected in torsional nanomechanical resonators similar to the those studied in Ref. [17] by measuring a deflection angle of a paddle attached to an armchair tube.

The discussion above ignored the backscattering part of the e-e interactions. The most relevant backscattering terms correspond to the so-called umklapp processes,
which transfer two right-moving electrons into left moving ones or vice versa. The bosonized form of the umklapp interaction can be written as

$$ H_u = -\frac{1}{2(\pi\varepsilon)^2} \int dx \cos(\sqrt{4\pi} \Phi_{c+}) $$

$$ \left\{ g_3 \cos(\sqrt{4\pi} \Theta_{c+}) + (g_3 - g_1) \cos(\sqrt{4\pi} \Phi_{c+}) \right\} $$

$$ + g_1 \left[ \cos(\sqrt{4\pi} \Phi_{c-}) - \cos(\sqrt{4\pi} \Phi_{s-}) \right] \right\}, $$

where the coupling constants can be expressed in terms of the matrix elements of the Coulomb interaction of electrons on the two sublattices with a large ($q \approx 2k_F$) and small ($q \approx 0$) momentum transfer: $g_3 = V_{AA}(2k_F) + V_{AB}(2k_F)$ and $g_1 = V_{AA}(0) - V_{AB}(0).$ In the absence of electron phonon coupling the umklapp processes lead to an insulating state with four different gaps for the different modes. The properties of the ground state and the magnitudes of the gaps depend on the values of the coupling constants $g_1$ and $g_3.$ These constants are very difficult to evaluate because they depend very sensitively on the short range part of the Coulomb interaction and on the spatial dependence of the electron density in the atomic orbitals. Within the model of point-like atomic orbitals and Coulomb interaction with a short distance cutoff numerical evaluation of the matrix elements gives $g_3 > g_1 > 0.$ In this case it is easy to see from Eqs. (19) and (3) that the umklapp processes compete with the twist instability. Indeed the umklapp interaction favors the condensation of the fields $(\Phi_{c+}, \Phi_{c-}, \Phi_{s+}, \Theta_{s-})$ in the ground state to $(0, 0, 0, 0),$ while the twist instability results in condensation of fields $(\Phi_{c+}, \Phi_{c-}, \Phi_{s+}, \Phi_{s-})$ to $(0, 0, \sqrt{\pi}, \sqrt{\pi})$ or $(\sqrt{\pi}, \sqrt{\pi}, 0, 0).$ We note that for $g_1 > g_3 > 0$ the umklapp processes enhance the twist instability and favor the ground state condensation pattern $(\Phi_{c+}, \Phi_{c-}, \Phi_{s+}, \Phi_{s-}) = (0, 0, \sqrt{\pi}, \sqrt{\pi}).$

For $g_1 > g_3 > 0$ the fate of the low temperature state thus depends on the relative strength of the e-ph and umklapp coupling constants. To estimate which ground state has the lowest energy one can compare the umklapp gap with that due to the twist instability. For $K_{c+} \ll 1$ the former scale as $\Delta_u \sim \frac{k_F^2}{\varepsilon}$ whereas the latter as $\Delta \sim \frac{g_3^2}{N}.$ Therefore in wide tubes the umklapp processes win. The outcome of the competition in narrow tubes depends on the values of the umklapp coupling constants. Theoretical estimates for the gaps range from tens to hundreds of Kelvins for $(5,5)$ tubes. Experimentally, armchair carbon nanotubes with $R \approx 0.8 \text{ nm}$ show no sign of the gap down to $T = 4K.$ Using $1/R^2$ scaling we infer that the umklapp gaps in $(5,5)$ armchair tubes should be below our estimates of $70K$ for the twist gap. These estimates suggest that twist instability may occur in freely suspended $(5,5)$ tubes. It could be observed by measuring the twist angle in the torsion resonators similar to those studied in Ref. [17].

We would like to thank David Cobden and Dam Son for useful discussions. This work was supported by DOE grants DE-FG02-07ER46452 (W.C. and A.V.A.) and DE-AC02-98 CH 10886 (A.M.T.), by the the BNL LDRD grant 08-002 (A.M.T.), and the US-Israel Binational Science Foundation grant No. 2004162 (D. O.).

[1] For a review, see R. Saito, G. Dresselhaus, and M. S. Dresselhaus, Physical Properties of Carbon Nanotubes (Imperial College Press, London, 1998).

[2] J.W. Mintmire, B.I. Dunlap, and C.T. White, Phys. Rev. Lett. 68, 631 (1992).

[3] M.T. Figge, M. Mostovoy, and J. Knoester, Phys. Rev. Lett. 86, 4572 (2001); Phys. Rev. B 65, 125416 (2002).

[4] H. Suzuura, and T. Ando, pp. 1625-1626, in Proc. of 25th Internat. Conf. on Phys. of Semiconductors. (Eds. N. Miura and T. Ando) (Springer, 2001).

[5] N. Viet, H. Ajiki and T. Ando, J. Phys. Soc. Jpn. 63, 3036 (1994).

[6] H. Ajiki and T. Ando, J. Phys. Soc. Jpn. 65, 505 (1996).

[7] D. Connetable, G.-M. Rignanese, J.-C. Charlier, and X. Blase, Phys. Rev. Lett. 94, 015503 (2005).

[8] C. Kane, L. Balents, and M. P. A. Fisher, Phys. Rev. Lett. 79, 5086 (1997).

[9] R. Egger and A. Gogolin, Phys. Rev. Lett. 79, 5082 (1997).

[10] A. Odintsov and H. Yoshioka, Phys. Rev. B 59, 10457 (1999).

[11] A.A. Nersesyan and A.M. Tsvelik, Phys. Rev. B 68, 235419 (2003).

[12] R. Jishi, M. S. Dresselhaus and G.Dresselhaus, Phys. Rev. B 48, 11385 (1993).

[13] G. Mahan, Phys. Rev. B 68, 125409 (2003).

[14] H. Suzuura and T. Ando, Phys. Rev. B 65, 235412 (2002).

[15] M. Ouyang, J. Huang, C. Cheung and C. Lieber, Science 292 702 (2001).

[16] D. Mann et al, Nano Lett., 3, 1541 (2003).

[17] A.R. Hall, et al, Phys. Rev. Lett. 96, 256102 (2006).

[18] O. Dubay, G. Kresse , and H. Kuzmany, Phys. Rev. Lett. 88, 235506 (2002).

[19] L. Balents and M.P.A. Fisher, Phys. Rev. B 55, R11973 (1997).

[20] T. Giamachi, Quantum physics in one dimension, Clarendon Press (2003).

[21] A.M. Tsvelik, Quantum Field Theory in Condensed Matter Physics, Cambridge 2003.

[22] H. Frohlich, Proc. R. Soc. London Ser. A 215, 291 (1952).

[23] S. Barisic, J. Labbé, and J. Friedel, Phys. Rev. Lett. 25, 919 (1970).

[24] S.G. Lemay, et al., Science 292, 617 (2001).

[25] A. De Martino, R. Egger, Phys. Rev. B 67, 235418 (2003).

[26] For large values of the coupling constant the forward scattering part of the e-ph coupling can become important and lead to the Bardeen-Wentzel instability. However, for values of the e-ph coupling quoted in the literature this does not occur even in the most narrow tubes, and accounting for this interaction leads only to inessential corrections to our treatment.