Twist Instability in Strongly Correlated Carbon Nanotubes

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We show that strong Luttinger correlations of the electron liquid in armchair carbon nanotubes significantly enhance the onset temperature of the putative twist Peierls instability and lead to its $1/R^3$ dependence on the tube radius. Depending on the values of the coupling constants the umklapp processes can either assist or compete with the twist instability. In the case of a 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 freestanding (5, 5) tubes.

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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 deformation modes are a lattice distortion with a finite wave vector [2] and the twist instability at zero wave vector [3,4]. Previous studies of this effect were carried out either in the noninteracting electron approximation [2–6], yielding a very low instability temperature $T_c \lesssim 0.1$ K, even for the thin (5, 5) nanotubes, or using *ab initio* calculations in the local density approximation (LDA) [7].

The purpose of the present work is to study the impact of electron-electron (e-e) interactions on this instability. The Luttinger liquid correlations, which cannot be captured within the LDA approach, are expected to be pronounced in armchair carbon nanotubes [8,9]. We find that the onset temperature for the *twist* Peierls instability is significantly enhanced by these correlations and scales as $1/R^3$ with the tube radius, in contrast to the exponential falloff that follows from the noninteracting electron approximation [3,4]. In the (5, 5) tubes T_c is enhanced by more than 2 orders of magnitude in comparison to the noninteracting electron result, and can be easily reached experimentally.

We also studied the interplay between the electron-phonon (e-ph) interactions and umklapp processes. In the absence of e-ph interactions the latter lead to a Mott insulating ground state [8–11]. While these processes can either enhance or compete with the twist instability, we find that for the theoretically estimated values of the umklapp coupling constants [10] the latter possibility is realized. As the strength of the umklapp scattering is increased to a critical value, the twist deformation of the lattice in the ground state vanishes discontinuously. The critical coupling strength may be estimated by equating the umklapp gap to the Peierls gap. Because of the slower, $1/R^2$, decay of the umklapp gaps with the tube radius, the umklapp processes win in wide tubes. In the narrow (5, 5) tubes we estimate the Peierls gap to be of the order of 70 K, based on the theoretical values of the e-ph couplings [12–14]. The umklapp gaps are much harder to evaluate theoretically because of their strong sensitivity to the short range part of e-e interactions [10,11]. Nevertheless, experiments indicate [15] that these gaps in the (5, 5) tubes are of the same order or below our estimates for the twist gap, suggesting the possibility of experimental observation of the twist instability.

We consider an undoped freestanding (N, N) armchair carbon nanotube; see Fig. 1(a). It has a symmetry 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, ± 1 [3]. The low energy electron spectrum is formed by two bands with opposite

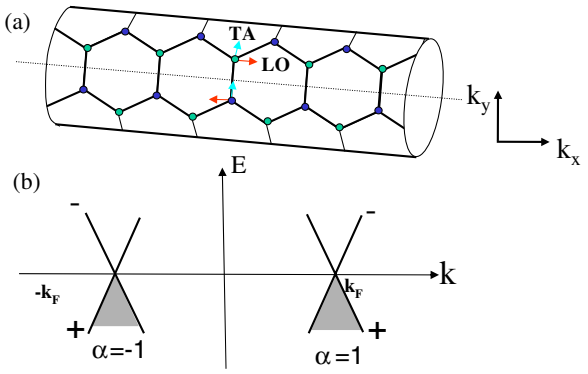

FIG. 1 (color online). (a) Schematic picture of an armchair tube. Light gray (green) and dark gray (blue) circles denote atoms in the A and B sublattices. The arrows show atomic displacements in the TA and LO phonon modes. (b) Free electron spectrum of armchair carbon nanotubes: + and − denote the parity of the bands. $\alpha = \pm 1$ corresponds to the two valleys with Fermi points at $\pm k_F$.

parity and zero angular momentum along the tube axis. These bands intersect at the two Dirac points as shown in Fig. 1(b).

Only phonon modes with zero angular momentum along the tube axis couple to the low energy electron modes. Furthermore, only the backscattering part of the 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 [16]. The backscattering by positive parity phonons involves large momentum transfer and corresponds to phonons with rather high frequencies, ~1000 K. This cuts off Luttinger liquid renormalization and results only in a finite softening of these phonons [17]. 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 longitudunal optical (LO) or radial optical (RO) [3,14]. The e-ph coupling arises from the change in the hopping matrix element induced by 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 by factor $1/N$ [14]. This relative smallness and the fact that its inclusion would only enhance the twist instability lead us to neglect it in the following analysis.

The phonon Hamiltonian can be written as

$$H_{\rm ph} = \frac{\rho}{2} \sum_{a=L,T} \sum_{q} [|\dot{u}_a(q)|^2 + \omega_a(q)^2 |u_a(q)|^2]. \quad (1)$$

Here ρ 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 $\omega_L(q) = \omega_o$ 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

$$H_{0e} = -i v_F \sum_{\alpha r \sigma} \int dx \psi^+_{\alpha r \sigma}(x) r \partial_x \psi_{\alpha r \sigma}(x), \quad (2)$$

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

The forward scattering part of the e-e interaction is much stronger than the backscattering part, the latter being small by $1/N$ [18]. The former can be written as

$$H_\rho = g_\rho \int dx n^2(x), \qquad n(x) = \sum_{\alpha r \sigma} \psi^+_{\alpha r \sigma}(x) \psi_{\alpha r \sigma}(x). \quad (3)$$

We assume that the Coulomb interaction is screened, e.g., by a gate at a distance d, where $d > R$, but short compared to the length of the tube L. Elementary electrostatics leads then to $g_\rho \approx 2e^2 \ln(d/R)$.

The above electron Hamiltonian is bosonized by the standard procedure (see, for example, Refs. [19,20])

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

Here $F_{\alpha\sigma}$ are the Klein factors, ξ is a short distance cutoff of the order of the radius of the nanotube, and Φ and Θ are boson fields satisfying the commutation relation $[\Phi_{\alpha\sigma}(x), \Theta_{\alpha'\sigma'}(x')] = -i\delta_{\alpha\alpha'}\delta_{\sigma\sigma'}\theta(x-x')$, with $\theta(x-x')$ being the step function. Introducing charge and spin modes combining different valleys,

$$\begin{aligned} \Phi_{\alpha\sigma} &= [\Phi_{c+} + \alpha\Phi_{c-} + \sigma\Phi_{s+} + \alpha\sigma\Phi_{s-}]/2, \\ \Theta_{\alpha\sigma} &= [\Theta_{c+} + \alpha\Theta_{c-} + \sigma\Theta_{s+} + \alpha\sigma\Theta_{s-}]/2, \end{aligned} \quad (5)$$

we rewrite the forward scattering part of the electronic Hamiltonian as

$$H_{0e} + H_\rho = \sum_j \frac{u_j}{2} \int dx [K_j^{-1}(\partial_x \Phi_j)^2 + K_j(\partial_x \Theta_j)^2]. \quad (6)$$

Here $j = c\pm, s\pm$, and the velocity and Luttinger parameter of the jth mode are related via $u_j = v_F/K_j$. For the three modes $j = c-, s\pm$, $K_j = 1$. For the charge mode $K_{c+} = 1/\sqrt{1 + 4g_\rho/\pi v_F}$. 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

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

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

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

By writing M in this form we adopted the convention $F^\dagger_{\alpha\sigma}F_{\alpha\sigma} = 1$. For $K_{c+} \ll 1$ the e-ph coupling (8) leads to a strong renormalization of the twist mode. To second order in the e-ph coupling the phonon propagator matrix becomes $\mathcal{D}(\omega_n, q) = [\mathcal{D}_0^{-1}(\omega_n, q) + \Sigma(\omega_n, q)]^{-1}$, where $\omega_n = 2n\pi T = 2n\pi/\beta$ is the Matsubara frequency, $\mathcal{D}_0^{-1}(\omega_n, q) = \delta_{a,a'}\rho[\omega_n^2 + \omega_a^2(q)]$ 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

$$\Sigma(\omega_n, q) = -P(\omega_n, q)\begin{pmatrix} g_T^2 q^2 & -ig_T g_L q \\ ig_L g_T q & g_L^2 \end{pmatrix}, \quad (9)$$

where $P(\omega_n, q) = \int dr e^{i\omega_n \tau - iqx}\langle M(0)M(r)\rangle$ and $\langle\cdots\rangle$ denotes thermal averaging with respect to the forward scattering Hamiltonian (6). In the bosonized representation it is given by

$$P(\omega_n, q) = \int \frac{2d^2 r}{(\pi\xi)^2} e^{i\omega_n\tau - iqx - (\pi/2)\sum_j \langle[\Phi_j(r) - \Phi_j(0)]^2\rangle}.$$

In the long wavelength limit, $q, \omega \to 0$, and for $K_{c+} \ll 1$ we obtain

$$P(0,0) \equiv P = \frac{1}{\pi^2 v_F}\left(\frac{\beta v_F}{\pi\xi}\right)^{1/2} B^2\left(\frac{3}{8},\frac{1}{4}\right), \qquad (10)$$

where $B(a, b)$ is the Euler beta function.

The renormalized phonon frequencies are given by the poles of $\det[\mathcal{D}(\omega_n, q)]$ analytically continued to real frequencies. The instability first appears when the renormalized frequency of the acoustic mode $\tilde{\omega}_T$ turns to zero

$$\tilde{\omega}_T^2 \equiv \omega_T^2 \frac{1-(\tilde{g}_T^2+\tilde{g}_L^2)v_F P}{1-\tilde{g}_L^2 v_F P} = 0, \qquad (11)$$

where $\tilde{g}_T = g_T/\sqrt{\rho s_T^2 v_F}$ and $\tilde{g}_L = g_L/\sqrt{\rho\omega_o^2 v_F}$ are the characteristic dimensionless e-ph coupling constants for TA and LO phonons, respectively. The mean field twist instability temperature is then

$$T_c = (\tilde{g}_T^2+\tilde{g}_L^2)^2 \frac{v_F}{\pi^5\xi} B^4\left(\frac{3}{8},\frac{1}{4}\right). \qquad (12)$$

In one dimension fluctuations shift mean field instabilities to zero temperature. In the case under consideration the order parameter $\partial_x u$ is real and the instability is of the Ising type. As a result, a finite order parameter exists only at $T = 0$, whereas at finite T one finds a state with a finite density of solitons (domain walls separating regions with different signs of $\partial_x u$). The mean field T_c is, however, not devoid of meaning and gives an estimate of the spectral gaps associated with the strong e-ph coupling. The exact composition of the excitation spectrum is currently unknown. Using the Feynmann variational principle we can estimate the magnitudes of the gaps of the singlet excitations of the fields Φ_j [19]. These excitations represent small fluctuations around the minima of the action. In addition to them there are also kinks which translate the fields between minima. More complete analysis of the spectrum will be given in an extended version of this Letter [21].

In the variational treatment of the condensed state [19] we assume that the lattice is statically deformed, $\partial_x u_T = \eta$, $u_L = \zeta$, and look for an electronic quadratic action $S_0 = (2\beta L)^{-1}\sum_j \sum_{\omega_n,q} G_j^{-1}(\omega_n, q)|\Phi_j(\omega_n, q)|^2$ which minimizes the variational electronic free energy $F_0 + T\langle S - S_0\rangle_0$, where $\langle\cdots\rangle_0$ denotes averaging with respect to S_0. The result is

$$S_0 = \frac{1}{2}\sum_j \int \frac{dx d\tau}{K_j u_j}[\dot{\Phi}_j^2 + u_j^2(\partial_x\Phi_j)^2 + \Delta_j^2\Phi_j^2], \qquad (13)$$

where, in the limit $K_{c+} \to 0$, the gaps Δ_j are given by

$$\frac{\Delta_j^2}{2K_j u_j} = \frac{1}{\xi}(g_T\eta + g_L\zeta)\prod_{j\neq c+}\left(\frac{\xi\Delta_j}{v_F}\right)^{1/4}. \qquad (14)$$

Minimizing the total variational free energy, including the elastic energy of the lattice, with respect to the static deformations ζ and η one obtains in the same limit

$$\eta = \frac{1}{\pi\xi}\frac{4g_T}{\rho s_T^2}\prod_{j\neq c+}\left(\frac{\xi\Delta_j}{v_F}\right)^{1/4}, \qquad (15)$$

$$\zeta = \frac{1}{\pi\xi}\frac{4g_L}{\rho\omega_o^2}\prod_{j\neq c+}\left(\frac{\xi\Delta_j}{v_F}\right)^{1/4}. \qquad (16)$$

Combining Eqs. (14)–(16) gives identical gaps for the four electronic modes,

$$\Delta_j = \frac{v_F}{\xi}\left[\frac{8(\tilde{g}_T^2+\tilde{g}_L^2)}{\pi}\right]^2, \qquad (17)$$

and a spontaneous twist angle of magnitude

$$\eta = \sqrt{\frac{2\pi}{1+(\tilde{g}_L/\tilde{g}_T)^2}}\frac{\Delta}{\sqrt{\rho s_T^2 v_F}}. \qquad (18)$$

In the framework of the tight binding model, the values of the coupling constants can be expressed [12,14,22,23] 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 found to be $g_T = \frac{\sqrt{3}}{4} a \frac{\partial J(r)}{\partial r}$ and $g_L = \frac{3}{2}\frac{\partial J(r)}{\partial r}$, where $a = 2.5$ Å is the graphene lattice constant, $c = 1.4$ Å the bond length, and $\frac{\partial J(r)}{\partial r} = -\lambda J_0/c$ with $J_0 = 2.6$ eV the hopping integral [24]. Here λ is a dimensionless constant whose theoretical value is 2 [13]. Theoretical calculations [3] give for the twiston phonon velocity $s_T \sim 1.4 \times 10^4$ m s^{-1} and for the LO phonon energy $\omega_0 \sim 0.18$ eV. The linear mass density of an (N, N) armchair nanotube is $\rho = 4NM/a$ with M being the carbon atom mass. Consequently, the dimensionless couplings $\tilde{g}_T$ and $\tilde{g}_L$ are proportional to $1/\sqrt{R}$, which in turn implies a $1/R^3$ scaling of the twist gap, Eq. (17). For a $(5, 5)$ armchair nanotube with $R \sim 0.35$ nm, our estimate for the transition temperature, Eq. (12), is about 40 K and the estimate for the gap, 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 $\eta \sim 3 \times 10^{-4}$ rad.

As mentioned above, solitonic effects will restore the symmetry at finite temperatures. However, if the length of the tube is shorter than the typical intersoliton distance, the system will appear twisted on experimental time scales. The estimated characteristic twist angle for $(5, 5)$ nanotubes, $\sim 0.01°$, 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 $x \sim 1$ μm. This twist can be detected in torsional nanomechanical resonators, similar to those studied in Ref. [25], 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 [8–11]. The bosonized form of the umklapp interaction can be written as [11]

$$H_u = -\frac{1}{2(\pi\xi)^2}\int dx \cos(\sqrt{4\pi}\Phi_{c+})\{g_3\cos(\sqrt{4\pi}\Theta_{s-}) + (g_3 - g_1)\cos(\sqrt{4\pi}\Phi_{s+}) + g_1[\cos(\sqrt{4\pi}\Phi_{c-}) - \cos(\sqrt{4\pi}\Phi_{s-})]\}, \quad (19)$$

where the coupling constants originate from the short range part of the Coulomb interaction, V_{AA} and V_{AB}, between electrons on the A and B sublattices. Explicitly, one finds $g_3 = V_{AA}(2k_F) + V_{AB}(2k_F)$ and $g_1 = V_{AA}(0) - V_{AB}(0)$ [10,11], both diminishing as $g_1, g_3 \propto 1/R$. In the absence of an e-ph coupling the umklapp processes lead to an insulating ground state. The gaps obtained within various approaches [10,11] differ by a numerical factor of order unity and for $K_{c+} \to 0$ scale as $\Delta_j \sim g_j/R$.

In the presence of an e-ph coupling the fate of the ground state depends on the values of the coupling constants. If $g_1 > g_3 > 0$ it is easy to see from Eqs. (19) and (8) that the umklapp processes and the twist instability cooperate and favor the same condensation pattern, $(\Phi_{c+}, \Phi_{c-}, \Phi_{s+}, \Phi_{s-}) = (0, 0, \frac{\sqrt{\pi}}{2}, \frac{\sqrt{\pi}}{2})$, for the bosonic fields. However, it is expected [10] that in nanotubes $g_3 > g_1 > 0$, leading to a competition between the twist instability and the umklapp processes, which in this case favor a different condensation pattern, $(\Phi_{c+}, \Phi_{c-}, \Phi_{s+}, \Theta_{s-}) = (0, 0, 0, 0)$. The outcome of the competition depends on the relative strength of the e-ph and umklapp coupling constants. Both variational and renormalization group treatments of the problem [21] show that as the umklapp coupling strength increases the system undergoes a discontinuous transition from the twisted state to a Mott insulator with an undeformed lattice. The transition occurs when the umklapp gap becomes comparable to the twist gap. For $K_{c+} \ll 1$ the former scale as $\Delta_u \sim \frac{v_F a}{R^2}$, whereas the latter as $\Delta \sim \frac{v_F a^2}{R^3}$. Therefore in wide tubes the umklapp processes win.

Our results imply that the twist instability may be realized in (5, 5) tubes, provided the umklapp gaps do not exceed a few tens of kelvin. Theoretical estimates [10] of these gaps range from tens to hundreds of kelvin for the (5, 5) tubes, and are difficult to ascertain because of their sensitivity to the details of the short range part of the e-e interaction. Gate voltage scans of the conductance of carbon nanotubes with $R \sim 0.85$ nm show no sign of a gap down to $T = 4$ K [15]. Using $1/R^2$ scaling, and assuming that the substrate and contacts do not change the tube parameters in a significant way, we infer that the umklapp gaps in (5, 5) armchair tubes should be below our estimate of 70 K for the twist gap. These estimates suggest that the twist instability may occur in freely suspended (5, 5) tubes.

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