Dark Soliton Excitations in Single Wall Carbon Nanotubes

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Abstract

Dark soliton excitations are shown to exist in single wall carbon nanotubes (SWCNTs). At first, the nonlinear effective interatomic potential and the difference equation for longitudinal lattice displacement are obtained for the SWCNTs by expanding Brenner's many-body potential in a Taylor series up to fourth-order terms. Then using a multi-scale method, for short wavelength lattice excitations the equation of motion of lattice is reduced to the cubic nonlinear Schrödinger equation. Finally, the dark soliton solutions and relevant excitations in the SWCNTs with subsonic velocity are discussed.

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Carbon nanotube (CNT) is the name of ultrathin carbon fiber with nanometer-size diameter and micrometer-size length and was accidentally discovered by Sumio Iijima [1] in 1991. As a novel and potential carbon material, CNTs have received a great deal of attention [2–6], and their many unique properties, such as structure [7–11], electronic property [12–14], superconductivity [15–18] and elementary excitations [18–22], have been investigated. The structure of the CNT consists of an enrolled graphite sheet, and can be classified into either multi-wall or single wall CNT (MWCNT or SWCNT) depending on its preparation method. The smallest SWCNT with a diameter of 4 Å was discovered in last year [23,24].

In recent years, there has been considerable efforts for studying the nonlinear localized excitations in lattices [25–27]. The nonlinear localized excitations can transfer energy and be involved in various processes of interest. There have been some speculations on the role played by solitary excitations in heat transfer, polymer destruction, and other processes occurring in molecular systems. The dynamical properties of the CNTs are of great interest due to their potential for useful practical applications [28]. The longitudinal soliton excitations governed by Korteweg-de Vries (KdV) equation in the CNTs using Brenner’s many-body potential have been investigated in Ref. [22]. Such solitons are obtained under the assumption of a long wavelength approximation. It is known that, in one-dimensional (1D) lattices, for a weekly nonlinear lattice excitation with a large spatial extension, its amplitude (or envelope) is governed by the nonlinear Schrödinger (NLS) equation when the excitation is a short wave wavepacket [29]. The nonlinear excitations in this case are envelope solitons. It is interesting to consider the envelope soliton excitations in the SWCNTs.

In this work we investigate the nonlinear effects in SWCNTs giving rise to dark envelope solitons using Brenner’s empirical many-body potential for carbon systems [30]. At first, we introduce a quasi-one dimensional lattice model for armchair (tube (m,m)) CNTs in an anharmonic approximation of the simple analytical Brenner’s potential. Then we derive a NLS equation by using a multiple-scale approach. Finally, we discuss the dark soliton solutions of the NLS equation and the physical relevance of these excitations in the SWCNTs.

The SWCNTs are highly anisotropic and ordered objects. The surface of the SWCNT
is formed by a graphite sheet folded into a cylinder with bond lengths and angles differing slightly from graphite on account of the strain induced by the folding. The interaction between adjacent atoms $i$ and $j$ in the SWCNTs can be described by the Brenner’s many-body potential [22], which reads

$$E_{ij}^b = V_{ij}^R - \bar{B}_{ij}V_{ij}^A,$$

where $V_{ij}^R$ and $V_{ij}^A$ are, respectively, exponential repulsive and attractive terms: $V_{ij}^R = 27.27 \exp[-3.28(r_{ij} - 1.39)]$ and $V_{ij}^A = 33.27 \exp[-2.69(r_{ij} - 1.39)]$. $\bar{B}_{ij}$ represents an environment dependent many body coupling between atoms $i$ and $j$ containing geometric information associated with the system. The total energy of the system is obtained by summation of Eq. (1) over all bonds. The energy and distances are measured in eV and angströms, respectively.

We take the cylindrical coordinate system $(R, \Phi, z)$ and align the tube axis as the $z$ axis so that $2m$ atoms in the SWCNT layer have the same $z$ coordinates. The equilibrium distance between layers, $l_0 = 1.26\,\text{Å}$ for a (5,5) tube.

Let us consider a cylindrically symmetrical disturbance in the SWCNT geometry as done in Ref. [22], in which all $2m$ atoms in the $n$th layer have identical $z$ and radical displacements from their equilibrium positions $Z_n^0$ and $R^0$: $Z_n = Z_n^0 + \zeta_n$ and $R_n = R^0 + \rho_n$, where $Z_n$ and $R_n$ are the perturbed coordinates and $\zeta_n$ and $\rho_n$ are the displacements from equilibrium positions. Then the coordinates of $i$th atom in $n$th layer are $(R^0 + \rho_n, \Phi_i^0, Z_n^0 + \zeta_n)$ for weak nonlinear excitations the $\zeta$ and $\rho$ are much smaller than the characteristic length scale. So the interatomic potential can be expanded in a Taylor series and the terms up to fourth order retained:

$$E = E_0 + \sum_{n=1}^{N_l} 2mE_n$$

where the $E_0$ is the ground state energy of relaxed SWCNT, $E_n = \frac{1}{2}(E_1 + E_2 + E_3)$ is the energy of an atom in the $n$th layer due to atomic displacements, where $E_1$, $E_2$ and $E_3$ are the energies of bonds emerging from any atom in the $n$th layer.
We rewrite the Brenner's potential (1) by expanding it in Taylor series up to the fourth-order terms as

\[
E(r) = \frac{A}{\sigma^2_2} \left( \sigma_2 \exp[-\sigma_1(r - r_0)] - \sigma_1 \exp[-\sigma_2(r - r_0)] \right)
\]

\[
= \frac{f}{2} (r - r_0)^2 - \frac{f}{3r_0} a_1 (r - r_0)^3 + \frac{f}{4r_0^2} a_2 (r - r_0)^4,
\]

(3)

where \( A = 27.27 \text{ eV}, \sigma_1 = 3.28 \text{Å}^{-1}, \sigma_2 = 2.69 \text{Å}^{-1} \) and \( r_0 = 1.39 \text{Å} \) and \( f = \sigma_1 A(\sigma_1 - \sigma_2) = 52.77 \text{eV}/\text{Å}^2 \). \( a_1 = \frac{r_0^2}{2} (\sigma_1 + \sigma_2) = 4.15 \) and \( a_2 = \frac{r_0^2}{6} (\sigma_1^2 + \sigma_1 \sigma_2 + \sigma_2^2) = 8.64 \). Thus \( E_i = E(r_i), i = 1, 2, 3 \) with

\[
r_1 = \{(R^0 + \rho_n)^2(\cos \Phi_{i+1} - \cos \Phi_i)^2 + (R^0 + \rho_n)^2(\sin \Phi_{i+1} - \sin \Phi_i)^2\}^{1/2} = r_0(1 + \rho_n/R^0),
\]

\[
r_2 = \{r_0^2 + (\rho_{n+1} - \rho_n)^2 + (r_0^2 - l_0^2)(\frac{\rho_{n+1} + \rho_n}{R^0} + \frac{\rho_{n+1} \rho_n}{(R^0)^2}) + 2l_0(\zeta_{n+1} - \zeta_n) + (\zeta_{n+1} - \zeta_n)^2\}^{1/2}
\]

and \( r_3 = r_2(n + 1 \to n - 1) \). Expanding \( r_2 \) and retaining the terms to the third-order, we get

\[
r_2 = r_0 + X_1 + X_2 + X_3,
\]

where

\[
X_1 = \frac{r_0^2 - l_0^2}{2R^0 r_0} (\rho_{n+1} + \rho_n) + \frac{l_0}{r_0} (\zeta_{n+1} - \zeta_n),
\]

\[
X_2 = \frac{1}{2r_0} (\rho_{n+1} - \rho_n)^2 + \frac{r_0^2 - l_0^2}{2r_0 (R^0)^2} \rho_{n+1} \rho_n - \frac{(r_0^2 - l_0^2)^2}{8r_0^2 (R^0)^2} (\rho_{n+1} + \rho_n)^2
\]

\[-\frac{(r_0^2 - l_0^2)l_0}{2r_0^2 R_0} (\rho_{n+1} + \rho_n)(\zeta_{n+1} - \zeta_n) + \frac{1}{2r_0} (1 - \frac{l_0}{r_0}) (\zeta_{n+1} - \zeta_n)^2,
\]

(4)

\[
X_3 = -\frac{1}{2r_0^2} \left( \left( \rho_{n+1} - \rho_n \right)^2 + \frac{r_0^2 - l_0^2}{(R^0)^2} \rho_{n+1} \rho_n + (\zeta_{n+1} - \zeta_n)^2 \right)
\]

\[\cdot \left( \frac{r_0^2 - l_0^2}{2R^0} (\rho_{n+1} + \rho_n) + l_0 (\zeta_{n+1} - \zeta_n) \right).
\]

Then we have

\[
E_n = \frac{r_0^2 f}{4(R^0)^2} l_0^2 - \frac{r_0^2 f}{6(R^0)^3} a_1 \rho_n^3 + \frac{r_0^2 f}{8(R^0)^4} a_2 \rho_n^4
\]

\[+ \frac{1}{2} f X_1^2 + f X_1 X_2 - \frac{f a_1}{3r_0} X_1^3 + f \left( \frac{1}{2} X_2^2 + X_1 X_3 - \frac{a_1}{r_0} X_1^2 X_2 + \frac{a_2}{4r_0^2} X_4 \right).
\]

(5)
If we neglect the radial degrees of freedom and reduce \( \zeta \) to the dimensionless unit \( \zeta \rightarrow \zeta_n / l_0 \), we get

\[
E_n = \frac{b}{2} (\zeta_{n+1} - \zeta_n)^2 - \frac{bp}{3} (\zeta_{n+1} - \zeta_n)^3 + \frac{bq}{4} (\zeta_{n+1} - \zeta_n)^4,
\]

where \( b = \frac{l_0^2}{r_0} f = 68.84 \text{eV}, \ p = -\frac{3}{2} (\frac{3}{2} + a_1) \frac{l_0^2}{r_0} = 3.14, \ q = \frac{1}{2} - (2a_1 + 3) \frac{l_0^2}{r_0} + (\frac{1}{2} + 2a_1 + a_2) \frac{l_0^4}{r_0^4} = 2.99 \). The equation of motion for longitudinal displacements reads

\[
\frac{d^2 \zeta_n}{dt'^2} = [\zeta_{n+1} - 2\zeta_n + \zeta_{n-1}] - p[(\zeta_{n+1} - \zeta_n)^2 - (\zeta_n - \zeta_{n-1})^2]
+ q[(\zeta_{n+1} - \zeta_n)^3 - (\zeta_n - \zeta_{n-1})^3],
\]

where we have made the dimensionless transformation for time \( t' = \sqrt{\frac{b}{(Ml_0^2)} t} \), M is the mass of carbon atom.

Now we investigate how the narrow band wave packets evolve by nonlinear effect \[29,31\]. We look for a solution expanded in terms of a small but finite parameter \( \varepsilon \) denoting the relative amplitude of the excitations:

\[
\zeta_n = \sum_{\nu=0}^{\infty} \varepsilon^{\nu+1} u^{(\nu)}_n
\]

and each \( u^{(\nu)}_n \) is also expanded in terms of harmonics \( \exp(il\theta_n) \) with "fast" variable \( \theta_n = k n l_0 - \omega t' \) as

\[
u^{(\nu)}_n = \sum_{l=-\infty}^{\infty} u^{(\nu)}_{n,l}(\tau, \xi_n) e^{il\theta_n}.
\]

where \( \tau \) and \( \xi_n \) are slowly varying variables defined by \( \tau = \varepsilon^2 t' \) and \( \xi_n = \varepsilon(n l_0 - \lambda t') \), respectively. \( \lambda \) denotes the group velocity \( \lambda = \frac{\partial \omega}{\partial k} \) which will be determined later. It is noted that the reality conditions

\[
u^{(\nu)}_{n,l} = \nu^{(\nu)}_{n,-l}^*
\]

should be satisfied for all \( \nu \) and \( l \).

Substituting Eqs. (8) and (9) into Eq. (7) and equating the coefficients of various powers of \( \varepsilon \) to zero, we get
\[
\sum_l \{-l^2 \omega^2 + 4 \sin^2 \left( \frac{l k \omega}{2} \right) \} u_{n,l}^{(0)} e^{i \theta_n} = 0,
\]
(11)

\[
\sum_l \left\{ 2i(l \omega - l_0 \sin l k l_0) \frac{\partial u_{n,l}^{(0)}}{\partial \xi_n} + (-l^2 \omega^2 + 4 \sin^2 \left( \frac{l k \omega}{2} \right) \} \right\} u_{n,l}^{(1)} e^{i \theta_n}
= p \sum_l \sum_{l'} 8i \sin^2 \left( \frac{l k l_0}{2} \right) \sin l' k l_0 u_{n,l}^{(0)} u_{n,l'}^{(0)} e^{i(l+l')\theta_n},
\]
(12)

\[
\sum_l \{(\lambda^2 - t^2 \cos l k l_0) \frac{\partial^2 u_{n,l}^{(0)}}{\partial \xi_n^2} - 2i l \omega \frac{\partial u_{n,l}^{(0)}}{\partial \tau} + 2i(l \omega - l_0 \sin l k l_0) \frac{\partial u_{n,l}^{(0)}}{\partial \xi_n} \}
+ (-l^2 \omega^2 + 4 \sin^2 \left( \frac{l k \omega}{2} \right) \} u_{n,l}^{(2)} e^{i \theta_n}
= p \sum_l \sum_{l'} 8i \sin^2 \left( \frac{l k l_0}{2} \right) \sin l' k l_0 (u_{n,l}^{(1)} u_{n,l'}^{(0)} + u_{n,l}^{(0)} u_{n,l'}^{(1)})
+ 8l_0 \sin^2 \left( \frac{l k l_0}{2} \right) \cos l' k l_0 u_{n,l}^{(0)} \frac{\partial u_{n,l}^{(0)}}{\partial \xi_n} + 4l_0 \sin l k l_0 \sin l' k l_0 \frac{\partial u_{n,l}^{(0)}}{\partial \xi_n} u_{n,l'}^{(0)} e^{i(l+l')\theta_n}
- q \sum_{l'} \sum_{l''} 4 \sin^2 \left( \frac{l k l_0}{2} \right) \{(e^{il'klo} - 1)(e^{il''klo} - 1) + (e^{il'klo} - 1)(1 - e^{-il''klo})
+(1 - e^{-il'klo})(1 - e^{-il''klo})\} u_{n,l}^{(0)} u_{n,l'}^{(0)} u_{n,l''}^{(0)} e^{i(l+l'+l'')\theta_n}.
\]
(13)

and the equations corresponding to higher order of \( \varepsilon \). To derive these equations, we have expanded the terms \( u_{n,l}^{(0)} \) in Taylor series of \( \varepsilon l_0 \), because \( \xi_{n,\pm 1} = \xi_n \pm \varepsilon l_0 \).

From above equations, we obtain the dispersion relation \( \omega^2 = 4 \sin^2 \frac{k l_0}{2} \), here \( k \) and \( \omega \) being respectively the wave number and the frequency of a lattice wave, and the following equations for the envelopes of the lattice wave

\[
u_{n,0}^{(0)} = 0, \quad \text{for } |l| \geq 2
\]
(14)

\[
\frac{\partial^2 u_{n,0}^{(0)}}{\partial \xi_n^2} = - \frac{8p}{l_0} \frac{\partial}{\partial \xi_n} \left| u_{n,\pm 1}^{(0)} \right|^2
\]
(15)

\[
i \frac{\partial u_{n,0}^{(0)}}{\partial \tau} = \frac{l_0^2}{8} \frac{\partial^2 u_{n,0}^{(0)}}{\partial \xi_n^2} + \omega \left\{ \frac{3}{2} \eta \omega^2 + p^2 (4 - \omega^2) \right\} \left| u_{n,1}^{(0)} \right|^2 u_{n,1}^{(0)} - pl_0 \omega \frac{\partial u_{n,0}^{(0)}}{\partial \xi_n} u_{n,1}^{(0)}.
\]
(16)

The Eq. (15) is easily integrated once and written as

\[
\frac{\partial u_{n,0}^{(0)}}{\partial \xi_n} = \frac{8p}{l_0} \left\{ \left| u_{n,1}^{(0)} \right|^2 - C \right\},
\]
(17)
where the $-\frac{8p}{l_0}C$ is an integration constant. Therefore from Eq. (16) we obtain the single equation to determine $u_{n,1}^{(0)}$

$$i \frac{\partial u_{n,1}^{(0)}}{\partial \tau} = \frac{l_0^2}{8} \omega \frac{\partial^2 u_{n,1}^{(0)}}{\partial \xi_n^2} + \omega \left\{ \frac{3}{2} \omega^2 - p^2 (4 + \omega^2) \right\} |u_{n,1}^{(0)}|^2 u_{n,1}^{(0)} + 8p^2 \omega C u_{n,1}^{(0)}. \tag{18}$$

By replacements of variables, we obtain the standard cubic nonlinear Schrödinger equation

$$i \frac{\partial \phi}{\partial z} = \frac{1}{2} \frac{\partial^2 \phi}{\partial x^2} - \kappa |\phi|^2 \phi \tag{19}$$

where $\phi = \exp(i8p^2\omega \int C d\tau)u_{n,1}^{(0)}$, $z = \omega \tau$, $x = \frac{2}{l_0} \xi_n$ and

$$\kappa = (p^2 - \frac{3}{2}q)\omega^2 + 4p^2. \tag{20}$$

Here $\kappa$ is always positive, because $p^2 - \frac{3}{2}q = 5.37 > 0$. It is known that the reversal of the sign of $\kappa$ leads not only to a change in the physics picture of the phenomena described by Eq. (19), but also to a considerable restructuring of the mathematical formalism necessary for its solution.

Now we investigate the modulational stability and solitons [32,33]. The NLS Eq. (19) has the simplest solution in the form of a continuous wave given by the expression,

$$\phi = \phi_0 e^{i\alpha x + i\beta z}, \quad \beta = \left(\frac{1}{2} \alpha^2 + \kappa \phi_0^2\right)$$

where $\phi_0$ is a constant. Let us investigate the linear stability of the exact solution, Eq. (21), against small perturbation as

$$\phi = (\phi_0 + \chi) e^{i(\alpha x + \beta z + \psi)}, \tag{22}$$

where the function $\chi$ and derivative of the phase $\psi$ are assumed to be small. Substituting Eq. (22) into Eq. (19), we look for the solution to these functions in the form, $\chi, \psi \sim \exp(i\Omega z - iQx)$, then obtain the dispersion relation as

$$Q^2 (\kappa \phi_0^2 + \frac{1}{4} Q^2) = (\alpha Q + \Omega)^2 \tag{23}$$

which means that the small excitation are always stable when $\kappa > 0$ and the small amplitude waves can propagate along the background. As a result, Eq. (13) has soliton solutions in
the form of localized "dark" pulses created on the continuous wave background. The NLS equation with the boundary conditions $|\phi| \to \phi_0$, at $x \to \pm \infty$, is exactly integrable by the inverse scattering method\cite{34},

$$\phi = \phi_0 (\cos \varphi \tanh \Theta + i \sin \varphi) e^{i \alpha x + i \beta z},$$

with $\Theta = \sqrt{\kappa} \phi_0 \cos \varphi [x - x_0 + (\alpha + \sqrt{\kappa} \phi_0 \sin \varphi) z]$, where $\phi_0$, $\varphi$, $\alpha$ and $x_0$ are free parameters. The $\phi_0$ is the amplitude, and $\varphi$ corresponds to the total phase shift across the dark soliton, $2\varphi$. Then we obtain

$$u_{n,1}^{(0)} = \exp(-i 8 p^2 \omega \int C d\tau) \phi$$

$$u_{n,0}^{(0)} = \frac{4p}{\sqrt{\kappa} \phi_0 \cos \varphi} \left[ (\phi_0^2 - C') \Theta - \phi_0^2 \cos^2 \varphi \tanh \Theta \right]$$

If we take $C = \phi_0^2$ for simplicity, then we obtain dark soliton excitations for the longitudinal displacement $\zeta_n$ up to the lowest order as

$$\zeta_n = A_0 \tanh \Theta [\cos X - \frac{2p}{M} - A_0 \tan \varphi \sin X]$$

with

$$X = (k + \frac{2}{l_0} \alpha') n l_0 - \left[ 2\alpha' \cos \frac{k l_0}{2} + (2 - \alpha'^2 - \frac{\kappa A_0^2}{2 \cos^2 \varphi} + \frac{4p^2 A_0^2}{\cos^2 \varphi}) \sin \frac{k l_0}{2} \right] \sqrt{\frac{b}{M l_0^2}} t,$$

$$\Theta = \frac{\sqrt{\kappa}}{l_0} A_0 [n l_0 - (\cos \frac{k l_0}{2} - (\alpha' + \frac{\sqrt{\kappa}}{2} A_0 \tan \varphi) \sin \frac{k l_0}{2}) \sqrt{\frac{b}{M}} t],$$

where $A_0 = 2 \phi_0 \varepsilon \cos \varphi$ is the rescaling amplitude and $\alpha' = \varepsilon \alpha$ is the rescaling parameter.

The velocity of the dark soliton is given by $v_g = [\cos \frac{k l_0}{2} - (\alpha' + \frac{\sqrt{\kappa}}{2} A_0 \tan \varphi) \sin \frac{k l_0}{2}] v_{\text{sound}}$, where $v_{\text{sound}} = \sqrt{b/M} = 22 \text{km/sec}$ is the longitudinal sound velocity, which means the velocity of dark soliton in the SWCNT is subsonic.

To summarize, We have obtained the nonlinear effective interatomic potential for the SWCNTs by expanding Brenner’s many-body potential in a Taylor series up to the fourth-order terms and the difference equation for longitudinal lattice displacements. Using the multi-scale method, for short wavelength excitations the equation of motion of lattice has
been reduced to the cubic nonlinear Schrödinger equation. We have discussed also the envelope dark soliton excitations in the SWCNTS. The dark soliton is the excitation of a dip excited on the continuous background of a high frequency harmonic oscillation of longitudinal displacement, and its velocity is subsonic. We note that the KdV soliton obtained in Ref. 22 is a weak nonlinear excitation valid only in a long wavelength approximation with a supersonic propagating velocity.

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