Collective excitations in metallic graphene tubules

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The collective modes of coaxial-graphene-tubule systems are calculated using both classical and quantum-mechanical approaches. While the derived results are valid for any number of coaxial tubules, the numerical results for the dispersion relations of the plasmons are presented for a system consisting of four graphene tubules for various values of the azimuthal quantum number m. The lowest modes ($m=0$) are found to be quasiacoustic, like the one-dimensional plasmons, whereas the higher modes are of optical nature. For each m, the number of observable modes is equal to the number of tubules having a metallic character. The effect of the intertubule interactions is a broadening of the frequency range of the m modes. This broadening remains important so long as the plasmon momentum is significantly smaller than the Fermi momentum.

The recent discovery[1,2] that the arc-discharge apparatus used for fullerene synthesis can also produce hollow tubules of graphitic carbons of up to a micrometer in length and several nanometers in diameter has led to much investigation of the properties of these nanotubes. It has been determined by electron-diffraction and microscopy experiments[1] that the tubules grow on the cathode of the discharge apparatus with their axes along the direction of the electric field and that a single needle can, in fact, consist of several coaxial tubules with the spacing between two successive tubes comparable to that between the layers of graphite. While the original experiments suggested that the ends of the tubules are closed off with carbon atoms arranged in pentagons,[3] recently it has been found[4] that occasionally these tubes can be open ended at least at one end. It is also known that the carbon-atom hexagons forming each tubule are, in most cases, arranged such that they form a helix about the tubule axis. More recently Ajayan and Iijima[5] have noticed capillarity-induced filling of the graphene tubules and have been able to produce lead wires of just two to three atoms across, giving credence to much speculation[6] about the possible applications of these graphitic structures.

The unusual structural characteristics of the nanotubes have prompted various theoretical investigations of their electronic properties. In three recent papers Mintmire, Dunlap, and White,[7] Hamada, Sawada, and Oshiyama,[8] and Saito *et al.*[9] have made first-principles calculations of the band structure of the graphene tubules. The former authors concluded from their local-density-functional calculation that some fullerene tubules may show a zero-band-gap or metallic behavior well below room temperature. The second group studied the variation of the band structures on the basis of the degree of helical arrangement of the carbon hexagons. In particular they have shown that if the configuration of the tubule is $B(2,1)N$ which corresponds to the axis of the tubule being normal to the C-C bond, the tubules will be metallic as was also found by Mintmire, Dunlap, and White[7] for a sample with $N=5$. Using a simple tight-binding model the third group obtained results which agree with those of Refs. 7 and 8. In a recent paper Lin and Shung[10] have calculated the elementary excitations of an electron gas confined in a cylindrical tubule within the random-phase approximation (RPA), and have presented numerical results for a single tubule and two coaxial tubules. However, their electron gas has an extremely low density compared to the metallic densities considered here.

In this paper we show that the theoretical study of the collective modes (plasmons) of a coaxial tubule system such as the graphene nanotubes can be performed by using either a classical or a quantum approach. The classical method presents certain advantages over a quantum calculation, such as the one performed by Lin and Shung.[10] These advantages are due to the particularly straightforward character of a classical calculation, which can, in fact, be extended rather easily to various situations such as increasing number of coaxial tubules, density of conduction electrons varying from tubule to tubule, background dielectric constants being different for the intertubule and the intratubule interactions, etc. Thus from a theoretical point of view, it is interesting to develop the classical methods of investigation of those tubules as far as possible paying special attention to their mesoscopic physical character. Such an approach is particularly suitable for the tubules having a metallic character.

However, the importance of the quantum approach should not be underestimated. First, it determines the range of validity of the classical description of the collective modes. Second, the damping of these modes is indeed related to the possible electron-hole pair excitations, which can be properly accounted for only in a quantum calculation. We will thus start by a short presentation and discussion of the quantum RPA calculation as applied to an isolated tubule.

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The one-electron states in a long tubule of radius a can be described by the two-dimensional (2D) wave function

$$1/(2\pi\sqrt{a})\exp(i\mathbf{K}\cdot\mathbf{x}) ,$$

where one has $\mathbf{K}\cdot\mathbf{x}=m'\phi+kz$ in cylindrical coordinates, the electron momentum being $\mathbf{K}=(m'/a,k)$ with the energy $E(\mathbf{K})=[(m'/a)^2+k^2]/2m^*$, m' being an integer (the azimuthal quantum number), and m^* the electron effective mass. If $\mathbf{Q}=(m/a,q)$ is the momentum transfer appearing in the (complex) dielectric function $\varepsilon(\mathbf{Q},\omega)$, the dispersion relations for the plasmon frequencies are obtained by solving $\mathrm{Re}\varepsilon(\mathbf{Q},\omega)=0$, or more precisely from

$$\varepsilon_0+V(\mathbf{Q})\,\mathrm{Re}\Pi(\mathbf{Q},\omega)=0 . \tag{1}$$

Here ε_0 is the background dielectric constant, and $V(\mathbf{Q})$ is the Fourier transform of the Coulomb potential in cylindrical coordinates having the following form:[11]

$$V(\mathbf{Q})=4\pi e^2 I_m(aq)K_m(aq) , \tag{2}$$

where I_m and K_m are the modified Bessel functions. $\Pi(\mathbf{Q},\omega)$ is the electron-hole propagator, the real part of which can be written in the usual form as

$$\mathrm{Re}\Pi(\mathbf{Q},\omega)=-2/(2\pi)^2\mathbf{S}_{\mathbf{K}}[\theta(E_F-E_-)-\theta(E_F-E_+)]\times(\omega-\Delta E)^{-1} , \tag{3}$$

where one has

$$\mathbf{S}_{\mathbf{K}}\cdots=\sum_{m'}\int d\mathbf{k}\cdots ,$$

$$E_F=k_F^2/2m^* ,$$

$$E_\pm=E(\mathbf{K}\pm\mathbf{Q}/2) ,$$

and

$$\Delta E=E_+-E_-=[mm'/a^2+kq]/m^* .$$

The summation-integration $\mathbf{S}_{\mathbf{K}}$ is performed over the occupied states as indicated by the step functions θ (which also means that the system is at zero temperature). The calculation of $\mathrm{Re}\Pi(\mathbf{Q},\omega)$ using (3) is rather straightforward, if we only keep the lowest-order term in ΔE, by assuming $|Q|\ll k_F$, i.e., replace $1/(\omega-\Delta E)$ by $\Delta E/\omega^2$. One then obtains

$$\mathrm{Re}\Pi(\mathbf{Q},\omega)=-Q^2R/(\pi^2m^*\omega^2) \tag{4}$$

with

$$R=\sum_{m=-m_0}^{m_0}\left[k_F^2-\left[\frac{m}{a}\right]^2\right]^{1/2} , \tag{5}$$

m_0 being the largest integer smaller than ak_F. The summation in (5) can be replaced by integration corresponding to a classical calculation if ak_F is large. One then obtains $R=\pi ak_F^2/2$, giving

$$\mathrm{Re}\Pi(\mathbf{Q}\omega)=-Q^2ak_F^2/(2\pi m^*\omega^2) . \tag{6}$$

Let us now show that the condition $ak_F\gg1$ is indeed satisfied in the metallic tubules and thus establish the range of validity of the classical calculation. In a 2D electron gas, the Fermi momentum is related to the 2D electron density n by $k_F^2=2\pi n$, and for a graphene tubule one has $n=\nu n_C$ where ν is the number of conduction electrons released per carbon (C) atom and $n_C=(4/3\sqrt{3})/s^2=0.38$ Å^{-2} is the density of C atoms [two C atoms per hexagonal units with s (=1.42 Å) as the C-C bond length]. From these expressions one obtains $k_F=1.55$ Å$^{-1}\sqrt{\nu}$. Note that for $\nu=1$ and an effective mass equal to the bare electron mass m_e, one obtains $E_F=9.14$ eV which is in good agreement with that of Mintmire, Dunlap, and White[7] who suggest $E_F=9.6$ eV. Concerning the radius a of the tubules we can use the results presented by Hamada, Sawada, and Oshiyama[8] who have shown that the most favorable structure for the metallic tubules is the $B(2,1)N$ structure (using the notations and indices proposed by these authors). This corresponds to a structure without helicity and with the C-C bonds perpendicular to the tubule axis. One then has $2\pi a=3Ns$ where N is an integer. These expressions for a and k_F give $ak_F=1.05N\sqrt{\nu}$, a quantity much larger than one, even for the smallest possible tubule ($N=5$). It is also interesting to mention that in a coaxial tubule system, the intertubule distance, yielded by theory and observation, is 3.39 Å, a distance that is to be compared with the distance 3.35 Å separating the graphene sheets in natural graphite.[12] This shows that from one adjacent tubule to another, N varies in steps of 5 units. This corresponds to a radius increment $\Delta a=(15/2\pi)s=3.39$ Å. The condition $ak_F\gg1$ is thus well satisfied and the summation in (5) can be replaced by an integration. Such an integration was not performed by Lin and Shung.[10] Indeed these authors consider tubules where the electron density is particularly weak (0.45 Å^{-1} per unit length), their charge carriers being introduced by intercalation. This corresponds to the weak 2D density, $n=0.11$ Å$^{-2}/N$. Since $N\geq5$, this density is smaller than the above metallic density $n\approx n_C=0.38$ Å^{-2} by at least one order of magnitude. The validity of the RPA may be questioned for such a low density.

Moreover, as we mention above, expression (4) of the electron-hole propagator is correct as long as $|\mathbf{Q}|$ is smaller than $k_F\approx1.55$ Å^{-1}. In other words, $q\Delta a$ or m cannot exceed $k_F\Delta a\approx5$, a number which will thus be the upper limit for the validity of the computation presented below regarding $q\Delta a$ and m.

From (1), (2), and (6), one obtains the dispersion relation $\omega=\omega_m(q)$ with

$$[\omega_m(q)]^2=(4\pi e^2na/\varepsilon_0m^*)Q^2I_m(aq)K_m(aq) . \tag{7}$$

For $m=0$ and $q\approx0$, (7) yields[13]

$$\omega_0(q\approx0)=\omega_p^a aq[2\ln(1.123/aq)]^{1/2} . \tag{7a}$$

This is a quasiacoustic mode having the dispersion relation of a one-dimensional plasmon.[14] Here the frequency

$$\omega_p^a=[4\pi e^2(n/2a)/\varepsilon_0m^*]^{1/2} \tag{8}$$

can be considered as the bulk plasmon frequency of an electron gas having a 3D density $n/2a$. For $q=0$ and $m\neq0$, using[13] $Q^2I_m(aq)K_m(aq)=m/2a^2$, one finds

$$\omega_m(0)=\omega_p^a\sqrt{m}\ . \tag{7b}$$

These modes ($m\geq 1$) present an optical character. These frequencies can be estimated numerically by assuming $\varepsilon_0=1$, $\nu=1$, $m^*=m_e$, and $a=\tau\Delta a$. One obtains

$$\omega_m(0)=\omega_p(m/\tau)^{1/2} \tag{7c}$$

with

$$\omega_p=[4\pi e^2(n/2\Delta a)/\varepsilon_0 m^*]^{1/2}=8.81\ \text{eV}\ . \tag{9}$$

The extension of this RPA calculation to a system of coaxial tubules requires the replacement of (1) by a more general expression involving an intertubule Coulomb potential[11]

$$V_{\tau\tau'}(\mathbf{Q})=4\pi e^2 I_m(qa_<)K_m(qa_>)$$

and propagators $\Pi_\tau(Q,\omega)$ related to each tubule τ ($a_<$ and $a_>$ are the smallest and largest tubule radius a_τ or $a_{\tau'}$, respectively). This requires a rather heavy calculation suggested in Ref. 10. However, we will now show how such a calculation can be cut short and extended by a systematic use of a classical model.

In a classical model one has to solve the following equation of motion:

$$m^*d^2/dt^2\mathbf{u}(\mathbf{x},t)=\nabla\int d^3x'(e^2/\varepsilon_0|\mathbf{x}-\mathbf{x}'|)\times n_v(\mathbf{x}')\nabla'\cdot\mathbf{u}(\mathbf{x}',t)\ . \tag{10}$$

For conduction electrons confined in coaxial tubules, the general density of electrons is given by

$$n_v(\mathbf{x})=\sum_\tau n_\tau\delta(r-a_\tau)\ , \tag{11}$$

where n_τ is the 2D-electron density on the τth tubule having a radius a_τ. Using the electron displacement $\mathbf{u}(\mathbf{x},t)=\mathbf{u}_0(r)\ \exp i(m\phi+qz-\omega t)$ in cylindrical coordinates, where $\mathbf{u}_0(r)$ is the 2D vector $[(m/r)U(r),qU(r)]$, (10) yields the secular equation

$$\omega^2U_\tau=\sum S_{\tau\tau'}U_{\tau'}\ , \tag{12}$$

where $U_\tau=U(a_\tau)$ and

$$S_{\tau\tau'}=(4\pi e^2/\varepsilon_0 m^*)n_{\tau'}a_{\tau'}[(m/a_{\tau'})^2+q^2]\times I_m(qa_<)K_m(qa_>)\ . \tag{13}$$

The eigenvalues $\omega^2=[\omega_m(q)]^2$ obtained by solving (12) represent the dispersion relation of the collective modes (plasmons) of the interacting tubule system.

For a general situation the solution of (12) becomes a computational problem which depends on the choice of the a_τ's and n_τ's. Before considering some particular situations, let us note that for each m value, the number of allowed modes is equal to the number of conducting tubules of the system, i.e., tubules with $n_\tau\neq 0$.

For $q=0$, $S_{\tau\tau'}$ simply becomes[13]

$$S_{\tau\tau'}=m(a_</a_>)^m[\omega_p^a\tau']^2\ , \tag{14}$$

where ω_p^a is defined by (8). Moreover, if we cancel the intertubule interaction by canceling the off-diagonal terms, we get expressions (7b) or (7a) for ω.

The most interesting and easiest tubule coaxial systems to investigate are those where the tubules have the $B(2,1)N$ structure. They all are assumed to have the same density n, and they are separated by the standard intertubule distance $\Delta a=(15/2\pi)s=3.39$ Å. In that case, one has $a_\tau=3sN/2\pi$ with $N=N_0+5\tau$ (τ being a positive integer and $N_0=0$, 1, 2, 3, or 4). We can assume $N_0=0$; this gives $a_\tau=\tau\Delta a$. We can then replace (12) and (13) by dimensionless expressions: ω is measured in ω_p-units, with ω_p given by (9), and $S_{\tau\tau'}$ becomes

$$S_{\tau\tau'}=\omega_p^2(2/\tau')[m^2+(z\tau')^2]I_m(z\tau_<)K_m(z\tau_>)\ , \tag{15}$$

with $z=q\Delta a$.

Let us now mention that to return to the noninteracting tubule system, we have just to cancel the off-diagonal terms of (15). Hence, one will have

$$[\omega_m(q)]^2=S_{\tau\tau} \tag{16}$$

which is in agreement with (7).

While the theory developed in this paper is valid for a system with any number of coaxial tubules, for the purpose of illustration we have carried out numerical calculations for a system with four coaxial tubules. The dispersion curves given by (7) or equivalently (16) for a noninteracting system are shown in Fig. 1, where an appropriate choice of units [ω is measured in (ω_p/τ) units and q in $(1/\tau\Delta a)$ units] yields "universal" curves independent of any choice of specific parameters such as τ. For $q=0$, one obtains (7a) or (7b) which are related to the

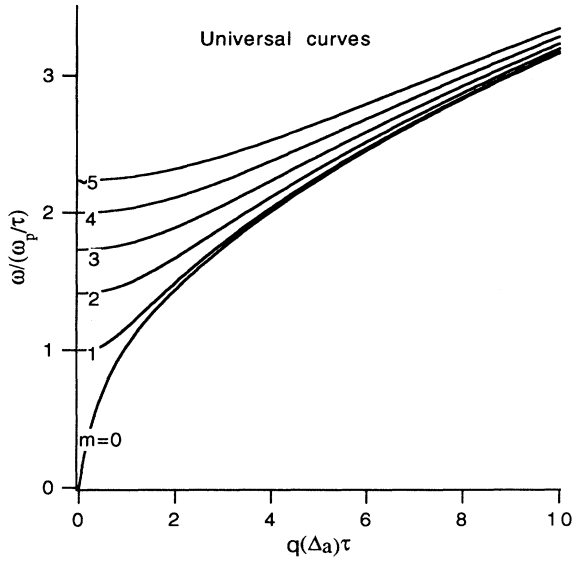

FIG. 1. The plasmon dispersion curves for an isolated tubule as given by (7). The lowest ($m=0$) mode is equivalent to a one-dimensional plasmon mode. For $q\approx 0$, it has a pseudoacoustic character as shown by (7a), whereas the other modes are optical in nature. Because of the use of appropriate units shown along the axes (with $a=\tau\Delta a$), these curves do not depend on any physical parameters.

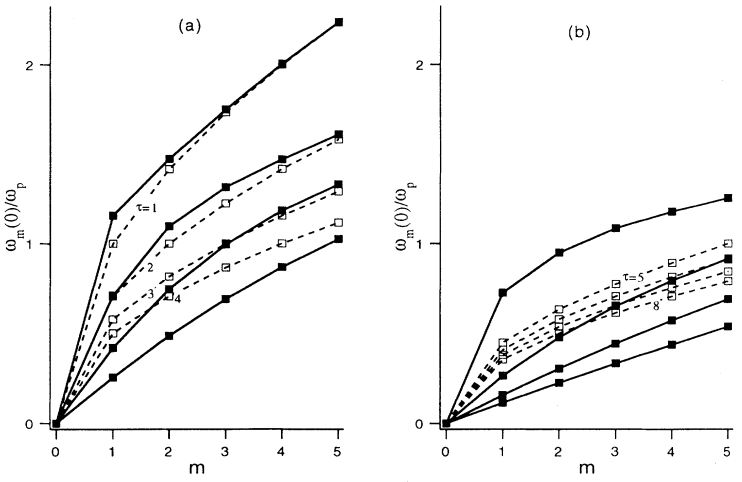

FIG. 2. The dispersion relations in (a) and (b) are related to the four-tubule systems I and II, respectively. They show the frequencies of the collective modes for $q=0$. The white squares are related to noninteracting tubules, the numbers τ indicating their radii $a_\tau=\tau\Delta a$. The black squares show the frequencies when the tubules interact. These latter frequencies are obtained by solving (12), using (14).

pseudoacoustic mode ($m=0$) or to the optical mode ($m\neq 0$), respectively.

In Fig. 2, we examine two particular systems (I and II). Both are constituted of four $B(2,1)3\tau$ tubules, all having the same density n of charge carriers. In system I, the radii of the tubules are given by $a_\tau=\tau\Delta a$ with $\tau=1,2,3,4$, and in system II by the same expression with $\tau=5,6,7,8$. First we consider the zero momentum situation which is depicted in Fig. 2(a) for system I, and in Fig. 2(b) for system II. The white squares connected by dashed lines are related to the noninteracting tubules, as indicated by the presence of the tubule indices τ. The ordinates of these white squares are the same as those of the starting points of the curves of Fig. 1 at $q=0$, as well as the ordinates of the black squares (and solid lines), which correspond to the interacting tubules. These latter points are obtained by solving (12), using (14). We note that the range of the frequencies (black squares vs white squares) becomes more extended, once the tubules interactions are switched on, and that this range is relatively more extended for

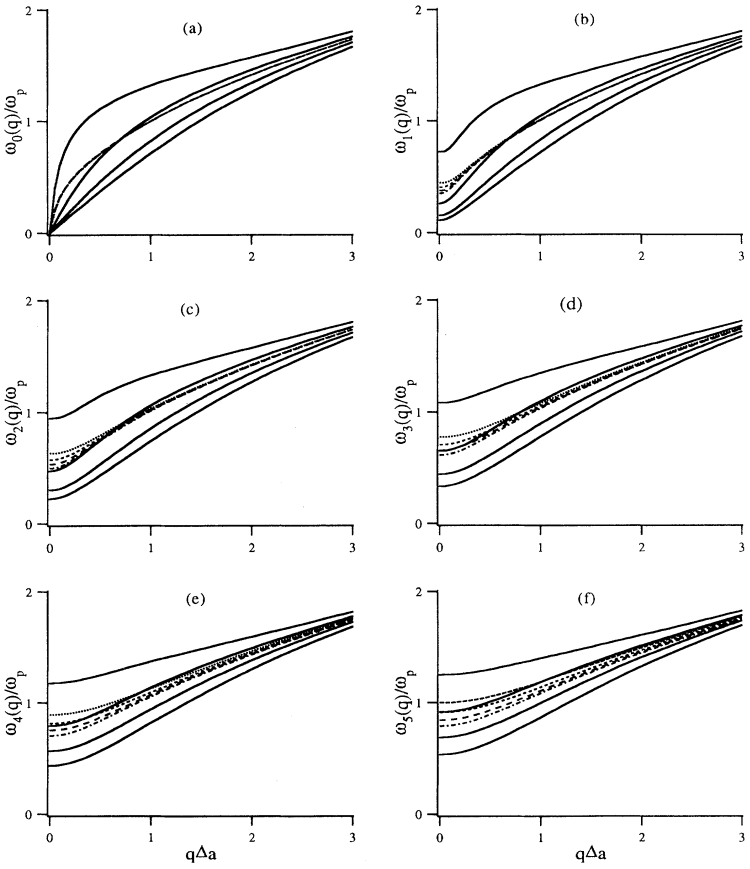

FIG. 3. These figures contain the dispersion curves for a four-tubule system with $\tau=5$. Each figure is related to a particular azimuthal quantum number m. The dotted and solid curves are related to the noninteracting and interacting systems, respectively. The effect of the interactions is a broadening of the frequency range, especially for $q\Delta a\leq 3$. As a reference momentum, one has $k_F\Delta a=5.25$, for one conduction electron released per carbon atom ($\nu=1$).

system I than for system II. This implies that the proper frequencies of the tubules are closer in system II than in system I, as shown by (7), and thus can resonate more easily. We also note that this resonant interaction is relatively stronger when m is small.

Figure 3 shows the effect of the interactions for $q \geq 0$. Each diagram of Fig. 3 shows the plasmon dispersion relation for a particular value of m and calculated for $\tau = 5$. We chose such a presentation of our results (rather than putting results of all m values in the same diagram), not only to avoid any confusion due to superposition of a number of curves belonging to different m's, but because the different m modes can be excited selectively by means of an incident radiation beam having the appropriate (circular) polarization. As expected we obtain four frequencies for each m, the broken lines being for the noninteracting case and the solid lines for the interacting case. We note that the effect of the tubule interactions becomes less important as q increases, as we have noticed a similar effect for increasing m. For $q\Delta a \geq 3$, this effect becomes negligible. As we have mentioned above, this corresponds to $q \geq 0.8$ Å^{-1}, which is half the Fermi momentum. Hence we are still in a region of the (q,ω) space where the plasmon excitations are not yet strongly damped by the electron-hole excitations, and thus should be observable. We also note that all curves of Fig. 3 tend to the same limit for q large. This (observable) limit can be obtained from the expression (15) for $S_{\tau\tau'}$ which becomes[13]

$$S_{\tau\tau'} = \omega_p^2 z \sqrt{(\tau'/\tau)} \exp(-z|\tau - \tau'|)$$

for z $(= q\Delta a)$ large, an expression independent of m. Moreover the off-diagonal terms become negligible. Hence for q large, all the dispersion curves represented in Fig. 3 tend to

$$\omega_m(q)/\omega_p = [q\Delta a]^{1/2} .$$

The two systems we have described are based on the same assumption: the density n of the charge carriers is the same in all the tubules. Actually that density may vary from tubule to tubule, depending on their radius of curvature a_τ.[8]

An experimental investigation of the evolution of the collective modes, with regard to the composition of the tubule system, should allow for the determination of the radius (and hence band structure) for which these tubules become metallic. The present theoretical analysis, and more particularly the dispersion relations established from (12) and (13), should facilitate such an investigation.

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