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LETTER TO THE EDITOR

Nondispersive and dispersive collective electronic modes in carbon nanotubes

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Abstract
We propose a new theoretical interpretation of the electron energy loss spectroscopy results of Pichler *et al* on bulk carbon nanotube samples. The origin of the nondispersive modes found experimentally has been controversial, and at least three different interpretations have been offered in the literature. From our theoretical results of the loss functions for individual carbon nanotubes based on a tight-binding model, we find that the nondispersive modes could be due to collective electronic modes in chiral carbon nanotubes, while the observed dispersive mode should be due to collective electronic modes in armchair and zigzag carbon nanotubes.

Carbon nanotubes have been centre-stage in physics research for over a decade, for good reasons. In addition to the long list of practical applications possible, the fundamental physical properties of carbon nanotubes have been extremely interesting and challenging. Notably, metallic carbon nanotubes have been found to exhibit Luttinger liquid behaviour [1], and whether a carbon nanotube is metallic or semiconducting is dependent on the chirality of the tubes. It is well known that, in a Luttinger liquid, single-particle excitations are suppressed; thus the collective electronic modes or plasmons play an extremely important role for carbon nanotubes.

Momentum-dependent electron energy loss spectroscopy (EELS) as carried out by Pichler *et al* [2–4] offers an excellent tool for studying plasmons in carbon nanotubes. Their experiment was performed first on bulk samples of single-wall carbon nanotubes [2, 3] and later on magnetically aligned bundles of single-wall carbon nanotubes [4]. In the low energy range of the spectrum, the experimental findings are: (i) a dispersive mode as a function of momentum transfer in the 5–8 eV range; (ii) several nondispersive modes at lower energies. The dispersive mode was attributed to the π plasmon without controversy. As for the nondispersive modes, no theory predicted their existence; Pichler *et al* first interpreted them in terms of interband excitations between localized states polarized perpendicular to the nanotube axis [2]. Later this interpretation was modified in the light of the new results coming from optical absorption measurements [5, 4, 9, 6–8].

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The bulk sample used in the experiment of Pichler *et al* had a mean diameter of 1.4 nm, and nondispersive modes were observed at 0.85, 1.45, 2.0, and 2.55 eV. Optical absorption measurements by Jost *et al* [5] on carbon nanotube-containing soot revealed excitations at 0.72, 1.3, and 1.9 eV for the mean diameter of 1.29 nm. Since the gap between van Hove singularities in the electronic density of states is known to be inversely proportional to the diameter, single-particle excitation energies should be larger in smaller diameter carbon nanotubes. However, the observed excitations in the experiment of Jost *et al* appear to be at smaller energies compared to those observed in the experiment of Pichler *et al*. To reconcile the two experiments, one has to assume that the nondispersive modes observed by Pichler *et al* are collective rather than single-particle modes. Additionally, recent experimental and theoretical results [6] on polarized optical absorption of aligned single-wall carbon nanotubes 1.35 nm in average diameter show that when the light is polarized parallel to the tube axis, the absorption spectra have several peaks below 3 eV, but when the light is polarized perpendicular to the tube axis, the absorption spectra become essentially featureless. Similar results were obtained earlier for tubes of much smaller diameter (0.4 nm) [7, 8]. These results suggest that the nondispersive modes are not due to excitations polarized perpendicular to the tube axis.

A recent paper by Liu *et al* [9] comparing optical absorption with EELS suggests that the nondispersive modes in the EELS are due to collective excitations of the optically allowed transitions. This could be a viable interpretation (barring the perpendicular polarization), making these modes analogous to the intersubband plasmons in quantum wires [10–12]. Although this interpretation seems to be more adequate, still no explanation was given for the nondispersive character. More theoretical work is necessary in order to further understand the experimental results.

The only way to explain the nondispersive character of the collective modes observed in the experiment theoretically is by studying their dispersion relations. Although many calculations are available in the literature for the momentum-dependent dielectric function and loss function of single- and multi-walled carbon nanotubes and bundles of single-walled carbon nanotubes [18, 17, 14, 15, 13, 16], only a few of them presented and discussed dispersion relations for the excitation modes [17, 14, 15, 13], and only one [17] tried to explain the origin of the nondispersive peaks observed by Pichler *et al*.

Three years after the initial experiment, theorist Bose [17] gave his explanation for the nondispersive character of the low energy peaks, noting that according to EELS theory [19], the experiment should measure the collective electronic modes and their dispersion relations. On the basis of a plasmon calculation using a model of a free electron gas confined to a cylindrical surface, he suggested an alternative interpretation of the nondispersive modes in terms of optical plasmons carrying nonzero angular momenta. However, a close inspection of the calculated plasmon dispersion curves presented in an earlier paper by Longe and Bose [18] reveals difficulties with this interpretation. In figure 1 of that paper, one can see that the acoustic plasmon which carries zero angular momentum is the lowest in energy and most dispersive. Plasmons with nonzero angular momenta are all optical, and as the angular momentum increases, the energy increases and the amount of dispersion decreases. While Bose did not clarify whether the dispersive mode corresponds to a zero-angular-momentum mode or not, difficulties arise regardless of how the dispersive mode is assigned: if it is assigned as a zero-angular-momentum mode, the optical plasmons should have *higher* energies than the dispersive mode, not at lower energies as experimentally observed; if it is assigned as a nonzero-angular-momentum mode, for the energies to be in the correct order, it must have larger angular momentum than the nondispersive modes, but larger angular momentum should correspond to less dispersion!

Clearly, over six years after the initial discovery of the nondispersive modes in EELS, the origin of the modes remains a puzzle. In this letter, we present our theoretical results on the loss functions of individual single-wall carbon nanotubes, and shed some light on the origin of the nondispersive modes. In particular, we propose that the nondispersive modes are inter(sub)band plasmons from chiral carbon nanotubes which have small Brillouin zones. These collective modes generally are not polarized perpendicularly to the tube axis. Further experiments are suggested for decisively determining the validity of this interpretation.

It is well known that the electronic properties of carbon nanotubes are dependent on the chirality. Whether a (n, m) carbon nanotube is metallic or not depends on whether the difference $n - m$ is divisible by 3. Such important details are not captured by a free electron gas type of model. On the other hand, a tight-binding model [20] is known to produce the electronic band structures of carbon nanotubes very well as long as the radius is not too small. We use such a tight-binding model for π band electrons to study the collective electronic excitations of individual carbon nanotubes—similar to the approach of Lin *et al* [14, 15]. The theoretical framework is the well used random phase approximation (RPA) theory, which has been applied successfully to many systems including quantum wires [10–12]. While this theory is usually used for Fermi liquids, Li *et al* [21] have shown that for a quantum wire with only one occupied subband, this theory gives the correct result for a Luttinger liquid. More recently, Que [22] has applied this theory to metallic carbon nanotubes, and obtained the same results as other established methods for studying Luttinger liquids. On the basis of these findings, it was concluded that the RPA theory is suitable for studying plasmons in both Fermi liquids and Luttinger liquids. Our numerical results for metallic tubes are consistent with the analytical results on Luttinger liquids [22].

Due to the cylindrical symmetry of the individual nanotubes, the electronic excitations have a well defined transfer momentum q_0 in the first Brillouin zone, angular momentum L, and energy ω; these dependences will be transferred to the dielectric matrix

$$\epsilon_{G,G'}(q_0, L, \omega) = \delta_{G,G'} - V_R(q_0 + G, L)\chi_{G,G'}(q_0, L, \omega) \tag{1}$$

where $V_R(q, L) = \frac{e^2}{\epsilon_0} I_L(|q|R)K_L(|q|R)$ is the 1D Fourier transform of the Coulomb interaction, I and K are the modified Bessel functions, R is the nanotube radius, e is the electron charge, ϵ_0 is the background dielectric constant, $\chi_{G,G'}(q_0, L, \omega)$ is the response function, and G, G' are lattice vectors in momentum space. The response function is calculated in the RPA within the tight-binding model, like in the Lin *et al* [14, 15] approach, but including the Umklapp terms, and the details will be presented elsewhere. The macroscopic dielectric function is given by [23]

$$\epsilon_{\mathrm{M}}(q_0, L, \omega) = \frac{1}{\epsilon_{0,0}^{-1}(q_0, L, \omega)}. \tag{2}$$

Figure 1 shows the loss functions of the (10, 10) armchair carbon nanotube (radius $R = 6.88$ Å), the (18, 0) zigzag carbon nanotube ($R = 7.15$ Å), and the (16, 3) chiral carbon nanotube ($R = 7.02$ Å). The angular momentum is a good quantum number and only the zero-angular-momentum modes are shown. Each loss function has several peaks but becomes featureless beyond 12 eV (σ band electrons are not included in the model).

Since L is a good quantum number, we have calculated the dispersions of collective electronic modes for different L values, and in figures 2 and 3 we show the $L = 0$ and 1 cases respectively. The dispersion curves terminate at the Brillouin zone edge of the corresponding carbon nanotube. In figure 2 we see that the (16, 3) tube has only optical modes, while the (10, 10) and (18, 0) tubes each have an acoustic mode. This is because the (16, 3) tube is semiconducting while the (10, 10) and (18, 0) tubes are metallic. Assuming a carbon–carbon

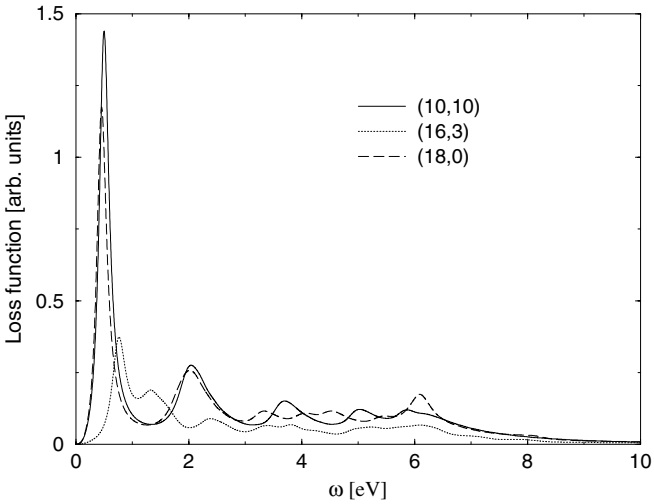

Figure 1. Loss function $\mathrm{Im}(-1/\epsilon_{\mathrm{M}}(q_0, L, \omega))$ computed for $q_0 = 0.04$ Å^{-1} and zero angular momentum ($L = 0$) for tubes with different chiralities but similar radii: about 7 Å. The (10, 10) armchair tube and the (18, 0) zigzag tube are both metallic. The (16, 3) chiral tube is semiconducting.

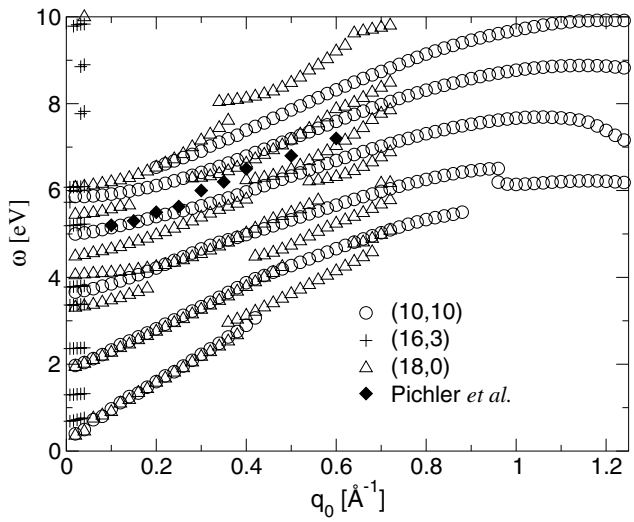

Figure 2. Dispersion curves for the collective electronic modes with angular momentum index $L = 0$, for the same three carbon nanotubes as in figure 1. The solid diamonds are experimental results on the dispersive mode from Pichler *et al*. The Brillouin zone edges for the (10, 10), (18, 0), and (16, 3) carbon nanotubes are at $q_0 = 1.26$, 0.73, and 0.041 Å^{-1}, respectively.

bond length of $a_{\mathrm{C-C}} = 1.44$ Å, it can be shown that all armchair carbon nanotubes have the same Brillouin zone edge of $\pi/T = 1.26$ Å^{-1} (T is the length of the translational vector [20]), and all zigzag carbon nanotubes have the same Brillouin zone edge of $\pi/T = 0.73$ Å^{-1}, but different chiral carbon nanotubes have different Brillouin zone sizes. Those (n, m) chiral nanotubes for which the greatest common divisor among $2n + m$ and $2m + n$ is 1 have the smallest Brillouin zones, with $\pi/T = \pi/(3a_{\mathrm{C-C}}\sqrt{n^2 + m^2 + nm})$. For the (16, 3) chiral

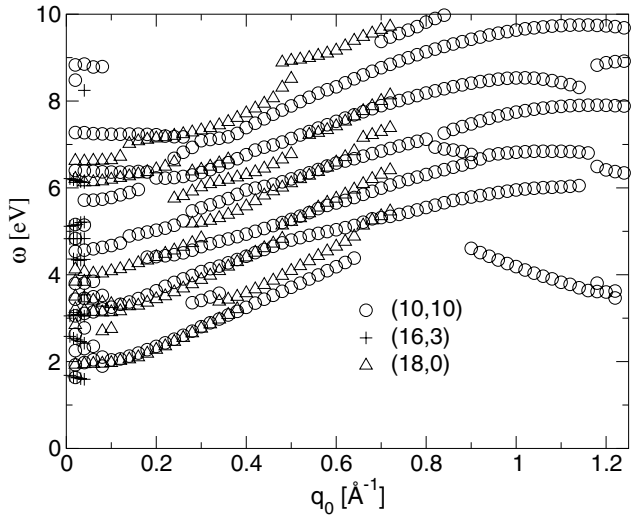

Figure 3. Dispersion curves for the collective electronic modes with angular momentum index $L = 1$, for the same three carbon nanotubes as in figure 1.

carbon nanotube, its Brillouin zone edge is at $\pi/T = 0.041$ Å^{-1}. Some of the curves for the (10, 10) and (18, 0) carbon nanotubes terminate before reaching the Brillouin zone edge due to vanishingly small peak amplitudes. Clearly, the (10, 10) armchair tube and the (18, 0) zigzag tube both have dispersive modes for all the L values of the computation, and we find this to be generally true for armchair and zigzag tubes. On the other hand, the collective electronic modes of the (16, 3) chiral tube have little dispersion, and this is also the case for many other chiral tubes. The reason for the lack of dispersion is the much smaller Brillouin zone.

If we compare the results in figures 2 and 3 with the results of Longe and Bose [18], we see that a major difference is that in the latter, there is only one branch of collective modes for each angular momentum index L, while in our results, we find many branches for each angular momentum index L, such as in figure 3. This is due to the band structures of carbon nanotubes with many occupied and empty (sub)bands. We find that when L is increased, excitation energies increase, and dispersion is reduced. Since the experimentally found dispersionless modes are at lower energies than the dispersive $L = 0$ π plasmon, one can rule out the possibility that they are $L > 0$ modes. We note that since the experiment of Pichler *et al* was performed on bulk samples (7 Å mean radius), the measured spectra contain contributions from many carbon nanotubes of different chirality. The nondispersive modes could be due to chiral carbon nanotubes, and the dispersive mode should be due to armchair and zigzag carbon nanotubes. Experimentally, only one dispersive mode was found, but since the peak of the dispersive mode was a couple of eV broad, it is possible that several modes of large amplitude contributed to the broad peak.

Since intertube coupling shifts the energies of the collective electronic modes higher [13], it is not possible to match the calculated energies in this work for individual carbon nanotubes to experimental results on bulk samples where intertube coupling is present. To allow an exact comparison between theory and experiment, it is desirable to obtain momentum-dependent EELS for individual carbon nanotubes, and such experiments should determine decisively the validity of the interpretation offered in this letter. We note that Reed and Sarikaya [24] have already done EELS work on individual carbon nanotubes (but not momentum-dependent

measurements) and noticed variations in results from different tubes. If our prediction is confirmed experimentally, eventually EELS could become a potential tool for identifying the chirality of individual carbon nanotubes.

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