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Plasma oscillations of the carbon peapod

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Abstract

We use a jellium model and the classical approach to study plasma oscillations of a carbon peapod. The dipole–dipole interaction between the C_{60} molecules in the array of C_{60} molecules encapsulated in a carbon nanotube is found to affect the longitudinal and transverse modes differently. The energy of the longitudinal mode is lowered, while the energy of the transverse mode is raised. The coupling between the nanotube and C_{60} molecules is found to be weak for longitudinal modes and strong for transverse modes. A carbon peapod is predicted to have Luttinger liquid behaviour similar to that of a carbon nanotube alone.

1. Introduction

The discoveries of the C_{60} fullerene [1] and carbon nanotubes [2] have triggered a great amount of research on these materials. More recently, it has been found that C_{60} molecules can be encapsulated in a carbon nanotube [3–5] and form a one-dimensional crystal within the nanotube [6, 7]. Such novel systems are called carbon peapods and their physical properties have not been fully understood. In this paper, we present a first attempt at understanding the plasmon excitations of carbon peapods. Plasmon excitations in carbon nanotubes and carbon peapods are extremely important. Electrons in metallic carbon nanotubes have been shown to exhibit Luttinger liquid behaviour [8–10]. In such nanotubes, at least for small wavevector q , single-particle excitations are forbidden, and the only possible excitations are collective modes—plasmon and spin density oscillations. The Luttinger parameter g of a Luttinger liquid [11] is the ratio between the single-particle excitation energy of a non-interacting Fermi liquid, and the plasmon energy of an interacting electron system, in the long-wavelength limit. In an armchair carbon nanotube, both of these energies are linear in wavevector q in the long-wavelength limit, giving a finite Luttinger parameter g . An intriguing question is whether this linear relation between the plasmon energy and wavevector q in the

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long-wavelength limit is destroyed in a carbon peapod, due to nanotube–C₆₀ coupling. A non-zero term independent of wavevector q in the plasmon energy would destroy the Luttinger liquid and make a Fermi liquid.

To understand the basic physics of carbon peapods without too many complications from a detailed model, we use a jellium model for carbon peapods and take a classical physics approach. Previously, the jellium model has been applied to the C₆₀ molecule [12, 13] and carbon nanotube [14] with reasonable results. In [12], it was shown that the jellium model agreed well with a tight-binding model for C₆₀ as far as the plasmon energy is concerned. Although our approach in general cannot be expected to explain experimental data in quantitative detail, the simplicity of the model and the approach makes it relatively easy to gain a qualitative understanding of the basic physics.

2. Model and results

We first discuss models for the constituents of a carbon peapod, the C₆₀ fullerene molecule, and a metallic carbon nanotube. These models are then combined to study the carbon peapod.

2.1. Fullerene molecule

The spherically shaped C₆₀ molecule has a diameter of $2R_f = 0.7065$ nm at 110 K [14]. We model the C₆₀ molecule by assuming that the charges of the 60 core ions are uniformly distributed on the surface of a sphere of radius R_f , and the charges of the N_f valence electrons are distributed homogeneously in a spherical layer $R_f < r < R$. The electrostatic potential arising from the valence electrons can be obtained as a solution of the Poisson's equation:

$$\nabla^2\varphi(\mathbf{r}) = -4\pi\rho(\mathbf{r}), \quad (1)$$

where ρ is the charge density, which is proportional to the density of the valence electrons n given by

$$n = 3N_f/4\pi(R^3 - R_f^3). \quad (2)$$

The angular frequency of the dipole oscillations of the valence electrons was estimated in [13]. Here we develop an improved approach to calculate electrostatic and kinetic energies of the motion.

Let us imagine that we fill the interior of the sphere with positive and negative electric charges of the same density as in the spherical layer. This does not change the real electrostatic potential and the energy of the system considered. The total (real plus imaginary) negative charge produces, according to Poisson's equation, the following potential inside the molecule ($e > 0$ is the electron charge):

$$\varphi(r) = \varphi(0) + \frac{eN_f}{2(R^3 - R_f^3)}r^2. \quad (3)$$

The total (real plus imaginary) positive charge of the fullerene molecule is

$$Q_p = eN_f R^3/(R^3 - R_f^3). \quad (4)$$

When the total negative charge is shifted relative to the total positive charge by a distance s , the change in electrostatic energy is

$$U = \frac{e^2 N_f^2 R^3}{2(R^3 - R_f^3)^2} s^2. \quad (5)$$

During oscillations, when $s(t) = s_0 \sin(\omega_f t)$, the time-averaged value of U is

$$\langle U \rangle = \frac{e^2 N_f^2 R^3}{4(R^3 - R_f^3)^2} s_0^2. \quad (6)$$

Now we evaluate the kinetic energy of the oscillations. Let us assume that the displacements u inside the electronic cloud are directed along the z -axis and

$$u(r, t) = \frac{r - R_f}{R - R_f} s_0 \sin(\omega_f t). \quad (7)$$

The local velocity v is directed along the z -axis also, and

$$v(r, t) = \frac{\partial u(r, t)}{\partial t} = \frac{r - R_f}{R - R_f} \omega_f s_0 \cos(\omega_f t). \quad (8)$$

The kinetic energy is equal to the integral over the volume of the electronic cloud of half of the product of the density $3mN_f/4\pi(R^3 - R_f^3)$ and the time-averaged value of v^2 :

$$\langle T \rangle = 0.25mN_f\omega_f^2 s_0^2 (0.6R^2 + 0.3RR_f + 0.1R_f^2)/(R^2 + RR_f + R_f^2). \quad (9)$$

According to the virial theorem, time-averaged values of the kinetic (equation (9)) and potential (equation (6)) energies of the oscillations for a linear harmonic oscillator should be equal. This yields

$$\omega_f = \frac{eR\sqrt{N_f R/m_f}}{R^3 - R_f^3}, \quad (10)$$

where $m_f = m(0.6R^2 + 0.3RR_f + 0.1R_f^2)/(R^2 + RR_f + R_f^2)$. The angular frequency given by equation (10) is larger than the one estimated in [13] by a factor of $[R^3/(R - R_f)(0.6R^2 + 0.3RR_f + 0.1R_f^2)]^{1/2}$. For $R = 0.538$ nm and $R_f = 0.353$ nm, this factor is 1.86.

The experimental value of $\hbar\omega_f$ is about 20 eV [16]. Taking $N_f = 120$ and $\hbar\omega_f = 20$ eV, and using equation (10), we come to the following equation for R (in atomic units):

$$2220R^3 = (R - R_f)^2 (R^2 + RR_f + R_f^2) (6R^2 + 3RR_f + R_f^2). \quad (11)$$

Numerical solution of equation (11) yields $R = 0.538$ nm for $R_f = 0.353$ nm.

2.2. Carbon nanotube

For a metallic carbon nanotube of length l , we assume that the charges of the N ions per unit tube length are uniformly distributed on the surface of a cylinder of radius R_n , and the charges of the N_n valence electrons per unit length $-eN_n$ are distributed homogeneously in a cylindrical layer $R_n < r < R_{ne}$. Plasma oscillations directed along the axis of a carbon nanotube were considered in [14]. It was shown there that the angular frequency of the oscillations is $\omega_{nl} = e(\pi N_n/lmR_{ne})^{1/2}$. This angular frequency is inversely proportional to the square root of the carbon nanotube length, suggesting that this plasmon is an acoustic mode. Other theorists also find this plasmon in a single nanotube to be acoustic [17–22], although in a carbon nanotube bundle this plasmon can become optical due to intertube Coulomb coupling [22].

2.3. Carbon peapod

As in [23] we assume that a periodic array of C_{60} molecules are encapsulated in a carbon nanotube, and there is interaction between valence electrons of a carbon nanotube and C_{60} molecules.

Low-energy plasma oscillations in a carbon peapod are longitudinal oscillations. Let us calculate the part of the electrostatic energy (per unit length) which depends on s and h , where s (h) is the shift between the total negative charge and the positive charge on a C_{60} molecule (carbon nanotube). It consists of the energy of the charges arising on the ends of a nanotube (see [14]),

$$U_1 = \frac{\pi e^2 N_n^2}{2l R_{ne}} h^2, \quad (12)$$

the energy of a fullerene molecule in equation (5) multiplied by the number of fullerene molecules in a unit length of a peapod n_f ,

$$U_2 = \frac{e^2 n_f N_f^2 R^3}{2(R^3 - R_f^3)^2} s^2, \quad (13)$$

the interaction energy of the dipole moments of the fullerene molecules $en_f N_f [R^3 / (R^3 - R_f^3)]s$ with the electric field inside a nanotube $\pi e(N_n / l R_{ne})h$ (see [14]),

$$U_3 = \frac{\pi e^2 n_f N_f N_n R^3}{l R_{ne} (R^3 - R_f^3)} sh, \quad (14)$$

and the energy due to dipole–dipole interaction in a periodic array of fullerene molecules,

$$U_4 = -\frac{2e^2 n_f^3 N_f^2 f(n_f l)}{l} s^2, \quad (15)$$

where $f(k) = \sum_{i=1}^{k-1} (k-i)/i^3$. U_4 is calculated in the approximation which neglects the size of a dipole. This approximation underestimates the effect of dipole–dipole interaction. The total electrostatic energy is the sum of the four terms and has the form

$$\begin{aligned} U(s, h) &= \frac{1}{2} A_l s^2 + \frac{1}{2} B_l h^2 + C_l sh, \\ A_l &= e^2 n_f N_f^2 [R^3 / (R^3 - R_f^3)^2 - 4n_f^2 f(n_f l) / l], \\ B_l &= \pi e^2 N_n^2 / l R_{ne}, \\ C_l &= \pi e^2 n_f N_f N_n R^3 / l R_{ne} (R^3 - R_f^3). \end{aligned} \quad (16)$$

Newton's equations [24] for all the valence electrons in a unit length of a carbon peapod are

$$\begin{aligned} m N_n \frac{\partial^2 h}{\partial t^2} + B_l h + C_l s &= 0, \\ m_f n_f N_f \frac{\partial^2 s}{\partial t^2} + A_l s + C_l h &= 0. \end{aligned} \quad (17)$$

Assuming $h = h_0 \sin(\omega t)$ and $s = s_0 \sin(\omega t)$, we obtain from equation (17) the following angular frequencies:

$$\omega_{pl1,2}^2 = \frac{1}{2} \left[(\omega_f^2 - 2\Omega^2 + \omega_{nl}^2) \pm \sqrt{(\omega_f^2 - 2\Omega^2 - \omega_{nl}^2)^2 + 4\pi n_f (R^3 / l R_{ne}) \omega_f^2 \omega_{nl}^2} \right], \quad (18)$$

where $\Omega^2 = 2e^2 n_f^2 N_f f(n_f l) / l m_f$, ω_{nl} is the angular frequency of the longitudinal oscillations in an isolated carbon nanotube, ω_f is the angular frequency of the plasmon in an isolated C_{60} molecule, and $\sqrt{\omega_f^2 - 2\Omega^2}$ is the angular frequency of the longitudinal plasma oscillations of a linear periodic array of C_{60} molecules. We find that the dipole–dipole interaction between the C_{60} molecules reduces the plasmon energy for longitudinal oscillations. We also find in this model that in a carbon peapod of infinite length, the coupling between the nanotube and C_{60} molecules becomes vanishingly small.

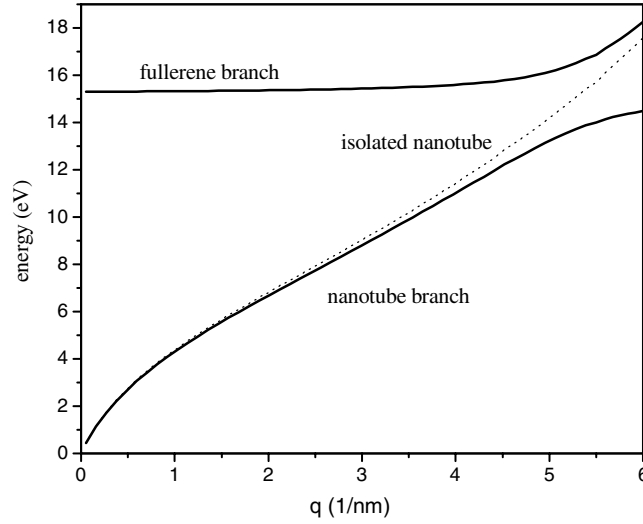


Figure 1. Plasmon energy as a function of wavevector q along the nanotube direction, for a carbon peapod of finite length. The dotted curve is the plasmon dispersion of an isolated carbon nanotube, from figure 2 of [22]. The lower (higher) solid curve is the nanotube (fullerene) branch, when coupling between the nanotube and C_{60} molecules is taken into account. We used the following parameter values: $\hbar\omega_f = 20$ eV, $N_f = 120$, $n_f = 1.03$ nm $^{-1}$ (from [6]), $N_n = 333$ nm $^{-1}$, $R = 0.538$ nm, $R_f = 0.353$ nm, $R_{ne} = 0.885$ nm, $R_n = 0.7$ nm, and $l = 29.1$ nm ($n_f l = 30$). With these values, we have $f(n_f l) = 34.4$, $\hbar\Omega = 9.07$ eV, $4\pi(n_f R^3/lR_{ne}) = 0.0783$, and $\hbar\sqrt{\omega_f^2 - 2\Omega^2} = 15.3$ eV.

Since ω_{nl} has been calculated by a full quantum theory in the random phase approximation [22], we can use results from such a theory to plug into equation (18). The plasmon in a linear array of fullerene molecules is expected to be almost dispersionless; thus we can use the value at zero wavevector. Figure 1 shows the coupled longitudinal modes in a finite-length carbon peapod, where the dotted curve is ω_{nl} obtained from figure 2 of [22]. For small wavevector q , the coupling between the nanotube and C_{60} molecules has a negligible effect, which implies that the carbon peapod should be a Luttinger liquid. In the vicinity of $\omega_{nl} = \sqrt{\omega_f^2 - 2\Omega^2}$, the coupling lowers the nanotube branch while it raises the fullerene branch, forming an anticrossing.

We have also considered transverse oscillations. In that case the total electrostatic energy is

$$U(s, h) = e^2 n_f N_f^2 [R^3/2(R^3 - R_f^3)^2 + n_f^2 f(n_f l)/l] s^2 + e^2 N_n^2 [R_{ne}^2/(R_{ne}^2 - R_n^2)] h^2 + 2e^2 n_f N_f N_n [R^3/(R_{ne}^2 - R_n^2)(R^3 - R_f^3)] s h. \quad (19)$$

The term $[e^2 n_f^3 N_f^2 f(n_f l)/l] s^2$ in equation (19) represents the energy of the dipole-dipole interaction between the fullerene molecules. Note that the corresponding term in equation (15) for the longitudinal case has a different sign and double the magnitude. We obtain the following angular frequencies for transverse oscillations:

$$\omega_{pt1,2}^2 = \frac{1}{2} \left[(\omega_f^2 + \Omega^2 + \omega_{nt}^2) \pm \sqrt{(\omega_f^2 + \Omega^2 - \omega_{nt}^2)^2 + 8(n_f R^3/R_{ne}^2)\omega_f^2\omega_{nt}^2} \right], \quad (20)$$

where $\omega_{nt} = eR_{ne}\sqrt{2N_n/m_n}/(R_{ne}^2 - R_n^2)$, $m_n = m(3R_{ne} + R_n)/6(R_{ne} + R_n)$. The quantity $\sqrt{\omega_f^2 + \Omega^2}$ is the angular frequency of the transverse plasma oscillations of the linear periodic

array of C_{60} molecules. In contrast to the longitudinal case, dipole–dipole interaction between the C_{60} molecules increases the plasmon energy for transverse oscillations.

For the same parameter values as in figure 1 and $\hbar\omega_{nt} = 43.4$ eV, we have $\sqrt{\omega_f^2 + \Omega^2} = 22$ eV, $8(n_f R^3/R_{ne}^2) = 1.66$, and equation (20) yields $\hbar\omega_{pt1} = 45.6$ eV, and $\hbar\omega_{pt2} = 16.9$ eV. For the transverse modes, the coupling between the nanotube and C_{60} molecules is independent of the tube length. The coupling between the nanotube and C_{60} molecules raises the energy of the transverse oscillations in the nanotube, while lowering that of the C_{60} array.

3. Discussion

We find that the dipole–dipole coupling between C_{60} molecules in a linear array affects the longitudinal and transverse modes differently: it lowers the energy of the longitudinal mode, while it raises the energy of the transverse mode. The coupling between the nanotube and the encapsulated C_{60} molecules is negligible for longitudinal modes in long carbon peapods. Its main effect in a finite-length carbon peapod is to cause an anticrossing between the nanotube and C_{60} array longitudinal modes. As for transverse modes, the coupling between the nanotube and the encapsulated C_{60} molecules is considerable and independent of tube length.

Calculations show that carbon peapods made of C_{60} molecules encapsulated in (n, n) armchair carbon nanotubes are generally metals [23]. For the (8, 8) and (9, 9) peapods, the energy bands crossing the Fermi level are similar to those of the corresponding carbon nanotube alone. For the (10, 10) peapod, four bands cross the Fermi level, instead of two bands in the case of a (10, 10) carbon nanotube. Single-walled (n, n) armchair carbon nanotubes have been known to exhibit Luttinger liquid behaviour [8–10]. Results from the present work imply that the Luttinger liquid behaviour should persist in a carbon peapod, and the Luttinger parameter g is not affected by the plasmon coupling between the nanotube and C_{60} . The value of g in a carbon peapod could still be different from that of a carbon nanotube, due to the change in the electronic band structure. For the (9, 9) and (8, 8) carbon peapods, the Luttinger parameter g should be essentially unchanged. For the (10, 10) carbon peapod, the Luttinger parameter g should be smaller than that for a (10, 10) carbon nanotube [25] assuming that the band structure in [23] is correct. The g -value for the (10, 10) carbon peapod can be estimated [25] to be approximately 30% smaller.

The simple approach used here provides a qualitative understanding of the basic physics, but a full, quantitative description requires a more detailed and quantum mechanical approach using the actual band structure. We are not aware of any experiments on plasmons in carbon peapods.

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