Optical properties of aligned carbon nanotube systems studied by the effective-medium approximation method

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(Received 3 September 1999; revised manuscript received 24 July 2000; published 28 December 2000)

Using the effective-medium approximation (EMA), which is valid for densely and randomly distributed particle composites, we have investigated optical properties of a dense carbon nanotube system, in which the nanotubes are parallel in orientation but random in position. The morphologies of both the Maxwell-Garnett theory (MGT) and the array model are not consistent with the dense and random character of this nanotube system. Comparing with the MGT and the array model, the EMA can describe better the experimental data. When the effect of the hollow core of the nanotubes are considered, the EMA results are still better and can describe the experimental data quite well.

DOI: 10.1103/PhysRevB.63.033401 PACS number(s): 78.66.Sq, 61.46.+w

I. INTRODUCTION

Tubular fullerenes have attracted much attention since their discovery in 1991,[1] and are made of a number of concentric cylinders of plane graphite. Because the graphite is highly anisotropic and its optical responses are quite different in the directions parallel and perpendicular to the normal axis of the graphite sheets, the carbon nanotubes are also highly anisotropic and their optical responses are very different in the directions along and normal to the nanotubes. So, materials including aligned carbon nanotubes may have highly anisotropic optical properties.

Recently, de Heer *et al.*[2] discovered a method to produce a thin film of aligned carbon nanotubes by drawing the tube suspension through a ceramic filter and then transferring the deposited material onto a plastic surface. Scanning electron micrographs of the surface show that the nanotubes are loosely and perpendicularly standing on the surface. After the surface is lightly rubbed with a thin Teflon sheet or aluminum foil, the nanotubes densely lie along the rubbing direction (i.e., parallel to the surface and almost parallel to each other). The films with the carbon nanotubes perpendicular and parallel to the surface are called β aligned and α aligned, respectively. Then, they measured the optical properties of these different tube aligned films. The α-aligned films are birefringent, reflecting differences in the dielectric function for light polarized along (s polarization) and normal (p polarization) to the nanotubes.

More recently, in order to obtain the effective dielectric function ε_{eff} of the α-aligned nanotube film, Garcia-Vidal *et al.*[3] proposed an array model in which infinitely long identical nanotubes are arranged parallel on a square lattice. By solving the Maxwell equations, they got Bloch waves possibly existing in the periodic system. Then, using the dispersion relation, they obtained ε_{eff} of the α-aligned film. For comparison, they also calculated ε_{eff} using the Maxwell-Garnett theory[4] (MGT), which describes effective dielectric properties of a granular composite with one kind of particles embedded randomly in a large volume of a host component. Both the array model and the MGT results can qualitatively but not well describe the experimental data in Ref. 2.

The effective medium approximation (EMA) (also called Bruggeman's theory)[5,6] is another method to describe the effective dielectric properties of composites in which the particles of all components randomly mix together. This theory has been widely used to explain the dielectric and optical properties of composite materials,[7–9] and proved valid at all concentrations.

The purpose of this paper is to show that the experimental data reported in Ref. 2 can be better described by the EMA than by the MGT or the array model in Ref. 3. The arrangement of this paper is as follows: In Sec. II, the basic ideas of the MGT and the EMA theories are given. In Sec. III, we calculate the effective dielectric function ε_{eff} of the α-aligned nanotube film using the EMA method and compare the obtained results with those of the MGT and the array model. Conclusions are drawn in Sec. IV.

II. FORMULATION

A. Dipolar polarizability of a single carbon nanotube

A local dielectric tensor of a cylindrical carbon nanotube can be described by

$$\varepsilon(\hat{r},\hat{\phi},\hat{z})=\varepsilon_{\parallel}\hat{r}\hat{r}+\varepsilon_{\perp}(\hat{z}\hat{z}+\hat{\phi}\hat{\phi}), \tag{1}$$

where $\hat{r}$, $\hat{\phi}$, and $\hat{z}$ are the base vectors of cylindrical coordinates, and $\varepsilon_{\parallel}$ ($\varepsilon_{\perp}$) is the principal component of the dielectric tensor of graphite parallel (perpendicular) to the normal axis of the graphite planes. This transfer procedure from the dielectric properties of planar graphite to nanotubes is justified because both of them are mainly sp^2 bonded.[10]

Under the quasistatic approximation, an external potential of the form $V_m(r,\phi)=V(r)e^{im\phi}$ will lead to the polarizability α_m of a single carbon nanotube per unit length[10]

$$\alpha_m = 4\pi\varepsilon_0\varepsilon_e R^{2m} \times \frac{(\varepsilon_\parallel\lambda-\varepsilon_i)(\varepsilon_\parallel\lambda+\varepsilon_e)\rho^{2m'}-(\varepsilon_\parallel\lambda-\varepsilon_e)(\varepsilon_\parallel\lambda+\varepsilon_i)}{(\varepsilon_\parallel\lambda-\varepsilon_i)(\varepsilon_\parallel\lambda-\varepsilon_e)\rho^{2m'}-(\varepsilon_\parallel\lambda+\varepsilon_e)(\varepsilon_\parallel\lambda+\varepsilon_i)}, \quad (2)$$

where $\rho = r/R$, $m' = m(\varepsilon_\perp/\varepsilon_\parallel)^{1/2}$ and $\lambda = m'/m$. r and R are inner and external radii of the nanotube and ε_i and ε_e are the dielectric functions of the internal and external materials, respectively. In deriving this expression, no field was assumed to be applied along the tube, and for external applied homogeneous field, $m=1$.

Now we introduce the anisotropic nanotube's equivalent isotropic dielectric function. Suppose a solid cylinder with an isotropic dielectric function ε and the same radius as the nanotube's external radius R. If this isotropic solid cylinder and the anisotropic nanotube have the same polarizability α_m under the same applied voltage, we call ε the anisotropic nanotube's equivalent isotropic dielectric function. For the isotropic solid cylinder, its polarizability α'_m can be easily deduced from Eq. (2) by letting $\varepsilon_\parallel = \varepsilon_\perp = \varepsilon$ and $\rho = 0$,

$$\alpha'_m = 4\pi\varepsilon_0\varepsilon_e R^{2m}\frac{\varepsilon-\varepsilon_e}{\varepsilon+\varepsilon_e}. \quad (3)$$

Then, if we let $\alpha'_m = \alpha_m$ in Eqs. (2) and (3), we can obtain ε, the equivalent isotropic dielectric function of the anisotropic nanotube.

B. Mean field theories

Assuming two kinds of solid particles in a binary composite have the isotropic dielectric functions ε_1 and ε_2, respectively, the average electric field $\vec{E}_{av}$ and electric displacement $\vec{D}_{av}$ of the composite can be written as

$$\vec{E}_{av} = f\vec{E}_1 + (1-f)\vec{E}_2 \quad (4)$$

and

$$\vec{D}_{av} = f\varepsilon_0\varepsilon_1\vec{E}_1 + (1-f)\varepsilon_0\varepsilon_2\vec{E}_2, \quad (5)$$

where f and $1-f$ are the volume fractions of the components 1 and 2 in the composite, and $\vec{E}_1$ and $\vec{E}_2$ are the average electric fields in components 1 and 2. The effective dielectric function ε_{eff} of the composite can be defined as

$$\varepsilon_{eff} \equiv \vec{D}_{av}/(\varepsilon_0\vec{E}_{av}). \quad (6)$$

1. MGT

When f is very small, each particle of component 1 can be treated as being embedded in a large medium of component 2. Therefore, the field $\vec{E}_2$ in component 2 is only slightly disturbed and approximately homogeneous, and by using Laplace's equation, the average inner electric field in the particles of component 1 can be written as

$$\vec{E}_1 = \frac{\varepsilon_2}{\varepsilon_2 + L(\varepsilon_1-\varepsilon_2)}\vec{E}_2. \quad (7)$$

Here, L is the depolarization factor of the particles along the principal axis that is parallel to the electric field $\vec{E}_{av}$. In a given dimension, the more slender the particle, the smaller the factor L. In three dimensions (3D), when the particle is spherical, $L=1/3$; and in 2D, when the particle is discal, $L=1/2$. Then, from Eqs. (4) to (7), we get

$$\varepsilon_{eff} = \varepsilon_2 + \frac{f\varepsilon_2(\varepsilon_1-\varepsilon_2)}{\varepsilon_2 + L(\varepsilon_1-\varepsilon_2) - fL(\varepsilon_1-\varepsilon_2)}. \quad (8)$$

This is the famous Maxwell-Garnett formula, which is generally used to treat dilute problems as it is derived from a dilute system. When $\varepsilon_2=1$, $L=1/2$, and $\rho=0$, Eq. (8) reduces to Eq. (5) in Ref. 3.

2. EMA

When f is not very small, the particles of the two components *randomly* mix together and the near neighbors of every particle in the composite include the two kinds of particles. We can no longer treat the particles of one component as being embedded in the other one, and it is impossible to get an exact result including the detailed interaction between the particles of the two components. An alternative way is to imagine that each particle in the composite is embedded in an infinite uniform medium with an effective dielectric function ε_{eff}, which will be obtained by a self-consistent procedure. The electric field outside each particle is treated as an average field $\vec{E}_{av}$ that is homogeneous, and has taken into account the complex interactions between the randomly dispersed particles.[11] Also, by solving the Laplace's equation, the average electric fields $\vec{E}_1$ and $\vec{E}_2$ in the two kinds of particles can be written as

$$\vec{E}_1 = \frac{\varepsilon_{eff}}{\varepsilon_{eff} + L(\varepsilon_1-\varepsilon_{eff})}\vec{E}_{av} \quad (9)$$

and

$$\vec{E}_2 = \frac{\varepsilon_{eff}}{\varepsilon_{eff} + L(\varepsilon_2-\varepsilon_{eff})}\vec{E}_{av}. \quad (10)$$

Substituting Eqs. (9) and (10) into Eq. (4), we obtain the following equation:

$$f\frac{\varepsilon_1-\varepsilon_{eff}}{\varepsilon_{eff}+L(\varepsilon_1-\varepsilon_{eff})} + (1-f)\frac{\varepsilon_2-\varepsilon_{eff}}{\varepsilon_{eff}+L(\varepsilon_2-\varepsilon_{eff})} = 0. \quad (11)$$

Equation (11) is the EMA formula. The derivation here is similar to that in Ref. 12. As a kind of mean-field theory, both Eqs. (8) and (11) are generally used to study random composites.

III. RESULTS AND DISCUSSIONS

In this part, we will discuss the optical properties of the α-aligned carbon nanotube films using the EMA method [Eq. (11)] and compare the obtained results with the MGT results [Eq. (8)] and the array model results in Ref. 3. Since the scanning electron micrographs show that the nanotubes are about parallel oriented for the α-aligned film, we can distinguish different situations for s and p polarization of light.

A. For *s*-polarized light

For s-polarized light, the electric fields are along the nanotubes. We let $L=0$, $\varepsilon_1=\varepsilon_\perp$, and $\varepsilon_2=1$, and then, Eqs. (8) and (11) reduce to

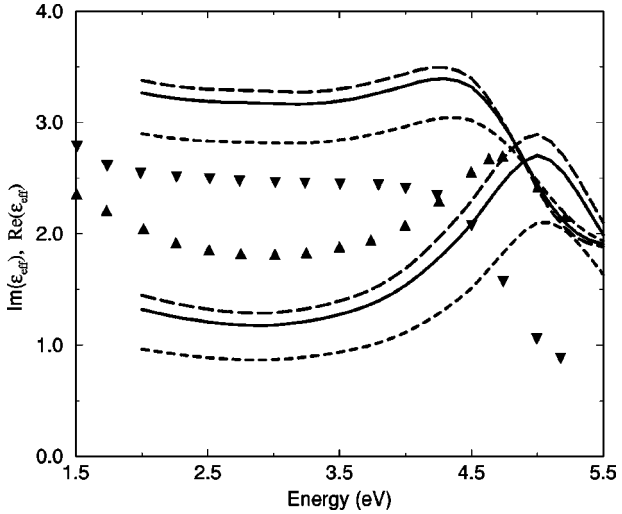

FIG. 1. The real and imaginary parts of the effective dielectric function ε_{eff} for *p*-polarized light for MGT method for different values of *f*. Long-dashed lines are $f \approx 0.74$. Solid lines are $f = 0.72$. Dashed lines are $f = 0.65$. The triangles up and down represent the imaginary and real parts of the experimental data in Ref. 2.

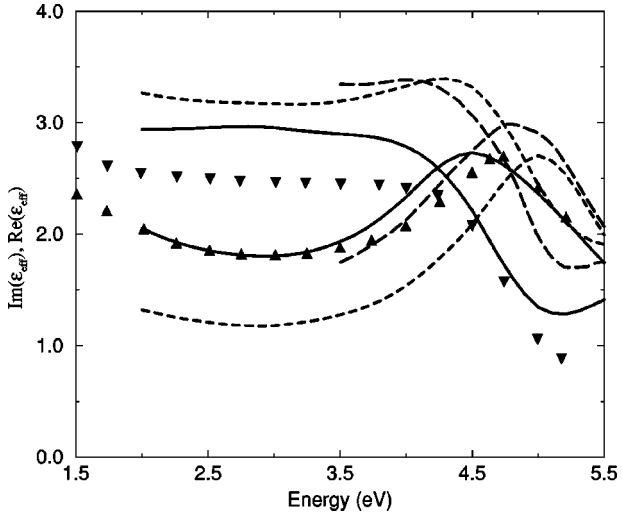

FIG. 2. The real and imaginary parts of the effective dielectric function ε_{eff} for *p*-polarized light for the array model, MGT, and EMA methods. Long-dashed lines: array model results at $d = 10.3$ nm (i.e., $f \approx 0.74$). Dashed lines are MGT results at $f = 0.72$. Solid lines are EMA results at $f = 0.67$. The triangles up and down represent the imaginary and real parts of the experimental data in Ref. 2.

$$\varepsilon_{eff}^{s} = f\varepsilon_{\perp} + (1-f). \tag{12}$$

Considering the hollow character of the tubes, we must replace the volume fraction f of the whole nanotubes in Eq. (12) by f' representing the volume fraction of the merely solid parts of the nanotubes. We assume all the structures of the nanotubes are the same and their internal and external radii are r and R. The solid part volume fraction f' can be expressed as

$$f' = (1-\rho^2)f, \tag{13}$$

where $\rho = r/R$. Then, the imaginary part of ε_{eff}^{s} is

$$\mathrm{Im}\,\varepsilon_{eff}^{s} = f'\,\mathrm{Im}\,\varepsilon_{\perp}. \tag{14}$$

Therefore, f' can be roughly estimated by comparing the maximum of known $\mathrm{Im}\varepsilon_{\perp}$ and experimental $\mathrm{Im}\,\varepsilon_{eff}^{s}$. Taking $R = 5$ nm and the internal radius r to be 0.25–2 nm, the value of $f \approx 0.6-0.7$ was obtained in Ref. 3.

B. For *p*-polarized light

For *p*-polarized light, its electric fields are perpendicular to the nanotubes. Because the lengths of the nanotubes are much longer than their diameters, the α-aligned nanotube film can be treated as a 2D random system. Then, in Eqs. (8) and (11), we let ε_1 denote the equivalent isotropic dielectric function of a single anisotropic carbon nanotube obtained from Eqs. (2) and (3), ε_2 denote the dielectric function of the air outside the nanotubes, and $L = 1/2$.

First, we assume all the nanotubes are solid cylinders. We have $\rho = 0$ in Eq. (2), and then, from Eqs. (2) and (3), ε_1 has its simple expression,

$$\varepsilon_1 = \sqrt{\varepsilon_{\parallel}\varepsilon_{\perp}}. \tag{15}$$

Using Eq. (8), the MGT results of ε_{eff}^{p} are obtained and shown in Fig. 1 for different volume fractions f of carbon cylinders. The triangles are experimental data. In our calculations, we have used the dielectric functions of graphite as tabulated in Ref. 13. It can be seen from Fig. 1 that both real and imaginary parts of the ε_{eff} decrease with the decreasing of f except in the vicinity of $E = 5$ eV, where the real part of $\varepsilon_{\perp}$ of graphite is negative. In the paper of Garcia-Vidal, they take the diameter of the nanotubes to be 10 nm and the distance between the nanotubes (i.e., period of the array model) to be 10.3 nm, (i.e., $f \approx 0.74$). The curves of their MGT results are shown as long-dashed lines. When f is 0.72, the peak of the imaginary parts of the MGT results approximately matches that of the experimental data in magnitude. Comparing with those at other volume fractions, the discrepancies of the real and imaginary parts between the MGT results and the experimental data seem to reach the minimum at this volume fraction. Even so, the discrepancies are still large. Besides their magnitudes, the real parts of the MGT results have distinct peaks in regions of $4.0 < E < 4.5$ eV, but this is not true for the experimental data. So, the MGT theory can only roughly describe the trend of the experimental data.

Then, we use the EMA theory by substituting Eq. (15) into Eq. (11). From the calculation, we found that, with a drop of f, the EMA results decrease just like the MGT results. In Fig. 2, we plot the EMA results of ε_{eff} in solid lines at $f = 0.67$, where the peak of its imaginary parts matches the experimental data in magnitude. Obviously, the EMA results can describe the experimental data better than the MGT results. Those redundant peaks in the real parts of the MGT results emerge no longer in those of the EMA results. As to the array model, Garcia-Vidal *et al.*[3] shifted the real parts of the experimental data approximately by an amount of one. We redraw the original curves of Garcia-Vidal *et al.*'s array model results (long-dashed lines) in Fig. 2 for comparison. It is clear that their results are far from satisfactory.

The above results can be understood as follows. It is well

known that morphology plays an important role in determining the optical properties of particle composites. For example, properties are quite different between composites with one kind of particles being dominantly surrounded by the other host component and composites with two kinds of particles randomly distributed. Obviously, both the array model and the MGT have morphologies consistent with the former composites, and therefore can give better descriptions, while the EMA describes the latter composites better.[14] In the α-aligned nanotube film in the experiment, the nanotubes might frequently contact each other. The air outside the nanotubes would be isolated by these contacting nanotubes and can be considered as ''particles'' of the air. So the morphology of α-aligned film is more like the latter one. Therefore, it is reasonable that the EMA better describes the α-aligned film because of the consistent morphologies of the theory and the system.

Second, we consider hollow tubes by assuming they have the same ratio ρ of inner to outer radii. Since $\rho \neq 0$, Eq. (15) can no longer be used, and ε_1 has to be obtained from Eqs. (2) and (3). According to the basis ideas of MGT and EMA, ε_e in Eqs. (2) and (3) should be replaced by ε_2 for MGT and ε_{eff} for EMA. From the calculation, we found that the equivalent isotropic dielectric function of a single nanotube changes lightly when $\rho < 0.2$. Then, we choose $\rho = 0.4$ for calculation. When the peaks of the imaginary parts of the theoretical results match that of the experimental data, we find, for both EMA and MGT methods, that the proper volume fractions are at about $f = 0.68$, which is consistent with the estimation of f for *s*-polarized light (see Sec. III. A, $f \approx 0.6$–0.7). Both the EMA and MGT results in this case are shown in Fig. 3. Comparing with Fig. 2, all the curves in Fig. 3 have similar trends to those in Fig. 2, but they are closer to the experimental data. The EMA can describe the experimental data quite well, especially in higher energy regions.

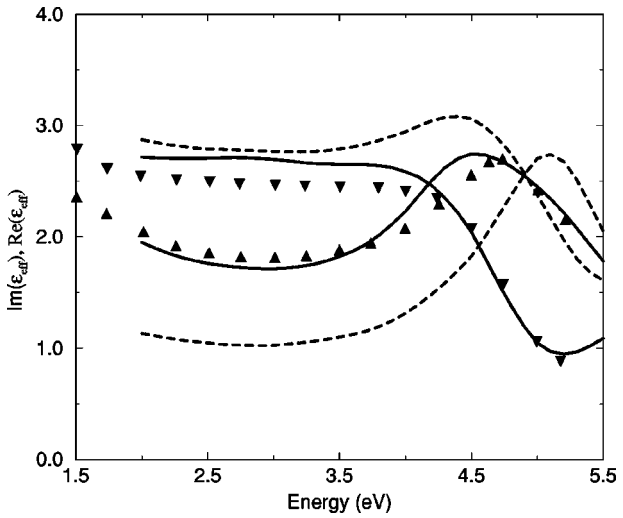

FIG. 3. The real and imaginary parts of the effective dielectric function ε_{eff} for *p*-polarized light obtained by the MGT and EMA methods for the hollow tubes with $r = 2$ nm and $R = 5$ nm. Dashed lines are MGT results at about $f = 0.68$. Solid lines are EMA results at about $f = 0.68$. The triangles up and down represent the imaginary and real parts of the experimental data in Ref. 2.

IV. SUMMARY AND CONCLUSIONS

By using the EMA theory, which is valid for densely and randomly distributed particle systems, and treating the nanotubes as solid cylinders with the equivalent isotropic dielectric functions, we have calculated the optical properties of the α-aligned nanotube systems and compared the EMA results with the MGT and the array model results. Our numerical calculations show that the EMA results can describe well the experimental data and are better than those of the array model and the MGT. In addition, we have included the effect of hollow tubes, and found both the EMA and MGT results are improved and, further, that the EMA results are better, indicating that the effect of the larger internal radii of the nanotubes cannot be neglected.

ACKNOWLEDGMENTS

The authors acknowledge support in this work from a grant by the State Key Program of China and support from the National Science Foundation of China through Grants No. 19674027 and 29890212, and the Natural Science Foundation in Jiangsu, Province of China, under Grant No. BK97022. J.D. also acknowledges support from a Grant RFDP.

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