PHYSICAL REVIEW B **71**, 104201 (2005)

Theoretical and computational studies of carbon nanotube composites and suspensions: Electrical and thermal conductivity

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(Received 3 June 2004; revised manuscript received 27 July 2004; published 4 March 2005)

Monte Carlo simulations have been performed, aimed at finding a critical fractional volume (CFV) associated with the onset of percolation for randomly oriented nanotubes (or, indeed, any conductive particles with large aspect ratios) that are randomly dispersed in a low thermo- or electroconductive medium. The nanotubes were treated as capped interpenetrating conductive cylinders ("sticks") with high (up to 2000) aspect ratio a. It has been found that for these aspect ratios the CFV is inversely proportional to a resulting in surprisingly low filler volume loadings, of the order of 0.01%, required to achieve percolation in such systems. By studying fluctuations of the CFV and the density of the percolation clusters, various critical indices of the percolation theory have been calculated including the critical index of conductivity, t. For three-dimensional systems it has been found that t decreases substantially with an increase in the aspect ratio. The calculated thermal and electrical conductivity of the nanotube suspensions and composites as functions of the nanotube loading is in good agreement with recent experimental data.

DOI: 10.1103/PhysRevB.71.104201 PACS number(s): 61.46.+w, 02.50.Ng, 64.60.Ak, 65.80.+n

I. INTRODUCTION

Carbon nanotube suspensions and composites have recently attracted much interest due to their possible technological applications: the addition of a very small amount of nanotubes substantially modifies the transport properties of the matrix (fluid) with no or little affect on its mechanical (hydrodynamic) properties.[1–5] Experimental studies of carbon-nanotube-in-oil suspensions[1] and carbon-nanotube-epoxy composites[2] show that their thermal conductivity is anomalously greater than that predicted by existing theoretical models (see Ref. 1 for references) and is nonlinear with nanotube loading. In comparison with other nanostructured materials (the so called nanofluids), including copper nanoparticles immersed in fluids, carbon nanotubes provide the highest thermal conductivity enhancement, with the conductivity ratio exceeding 2.5 at approximately 1% of nanotube volume fraction.[1] In addition, measurements of the thermal[1,2] and electrical[3–5] conductivities of nanotube suspensions[1] and composites[2–5] reveals a negligibly small percolation threshold [critical fractional volume (CFV)] for these materials. Based on these findings, attempts were made to explain the conductivity of the materials in question using the framework of conventional effective-medium models of solid/liquid suspensions (see Ref. 1 for details), for which the CFV is equal to zero. These models failed, however, to adequately describe the experimental data on thermal conductivity of carbon-nanotube suspensions.[1] They obviously cannot account for the recently observed[4,5] percolation scaling law that describes the electrical conductivity of the composite materials as the carbon nanotube content is increased. By means of Monte Carlo simulations we will demonstrate that, in materials with conductive filler made of particles with sufficiently large aspect ratios, percolation theory can well explain both the very low-conductivity thresholds and the nonlinear dependence of the conductivity on the filler loading.

In Sec. II, we will describe computational and theoretical procedures for finding the critical fractional volume of nanotube composites. In Sec. III, by studying the fluctuations of the CFV and the density of the percolation clusters, we will calculate the basic critical indices governing the behavior of these clusters. In Sec. IV, the scaling hypothesis will be used to estimate the preexponential factor in the expression for the conductivity. And finally, in Sec. V we will apply percolation theory to analyze the electrical and thermal conductivity of systems comprising interconnected carbon nanotubes immersed in a low-conductive medium above the percolation threshold.

II. CALCULATION OF THE CRITICAL FRACTIONAL VOLUME

We have developed Monte Carlo simulation code aimed at finding the CFV of nanotubes (or any oblong conductive particles) suspended in a low thermo- or electroconductive medium. The code works as follows. A certain number N (smaller than the critical one) of capped cylinders (spherocylinders or sticks) of a given length l and diameter d (see Fig. 1) are randomly planted in a unit cube (both l and d are

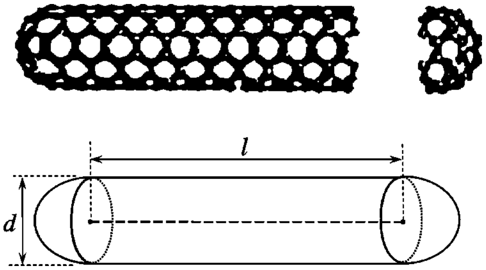

FIG. 1. Carbon nanotube and its representation as a capped cylinder.

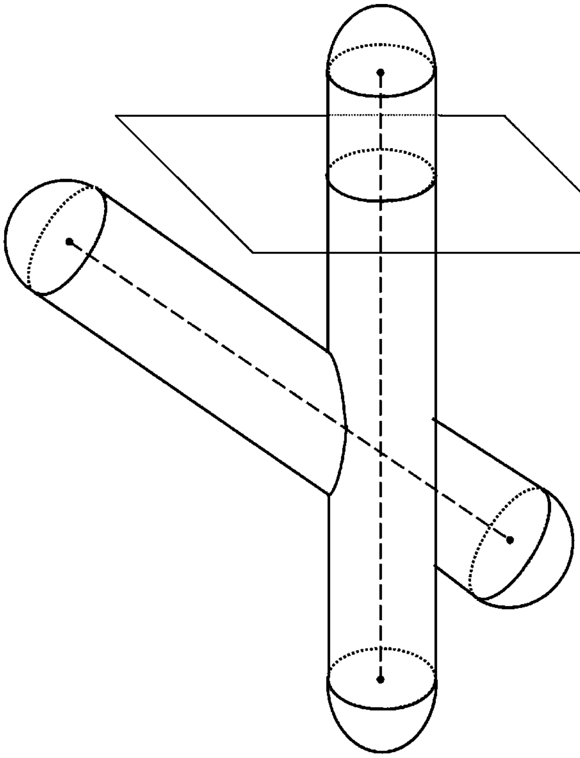

FIG. 2. Intersections of two capped cylinders.

measured in the units of the unit cube size). The centers of mass of these sticks are given random coordinates, and the two angles, azimuthal, θ, and polar, φ, specifying the orientation of their axes are randomly distributed within the intervals $(0,\pi/2)$ and $(0,2\pi)$, respectively. To assure the correct isotropic orientation of the nanotubes in the whole range of solid angle, the ends of the sticks must span uniformly the surface of a sphere. This can be achieved by choosing a weighted distribution for the azimuthal angle: $f(\theta)=\sin\theta$ (see Ref. 6 for details).

For the sake of computational simplicity, the sticks are considered to be interpenetrating or soft core. (We will discuss this assumption later on in this section and we will show that it is not significant for objects with large aspect ratio.) As sticks are added the code determines which, if any, of the existing sticks are intersected by the new stick, and whether the new stick crosses the boundary of the unit cube (Fig. 2). The code also updates (if necessary) the clusters formed by the sticks. Finally, it verifies if a percolation cluster has been established, which connects opposite sides of the cube. If this cluster is not detected, new sticks are added in small increments until percolation is achieved at a critical concentration, $\tilde{N}_c(l;a)$. For a given l and d (or l and the aspect ratio $a=l/d$) the simulation was repeated up to a hundred times in order to find the value of the critical concentration, $N_c(l;a)=\langle\tilde{N}_c(l;a)\rangle$, averaged over different realizations of the percolation cluster.

For a given aspect ratio a, this procedure was repeated for successively increased size of the system or, which is equivalent, for diminished size of the length l of the sticks and their diameter $d=l/a$. The thermodynamic limit of the total critical volume, $V_c(a)$, contained in all such sticks has been evaluated by means of the following extrapolation formula:

$$V_c(l;a)=\langle\tilde{N}_c(l;a)\rangle V(l;a)=V_c(a)+Al^{\lambda}. \tag{1}$$

Here A and λ are constants and

$$V(l;a)=\frac{\pi(2+3a)}{12}\left(\frac{l}{a}\right)^3 \tag{2}$$

is the volume of a capped cylinder (Fig. 1). Then the CFV can be calculated as (see Refs. 7 and 8 for details)

$$\phi_c=1-\exp[-V_c(a)]. \tag{3}$$

The CFV in Eq. (3) actually represents the probability of a random point being inside any stick for a system of identical interpenetrating sticks on the verge of the percolation threshold. Figure 3 shows the procedure for finding the thermodynamic limit of the total critical volume, $V_c(a)=\lim_{l,d\to 0}V_c(l;a)$, for systems of identical sticks with different aspect ratios. It can be seen that $V_c(l;a)$ approaches its thermodynamic limit in a different way for three-dimensional (3D) systems comprising round $(a\lesssim 1)$ and oblong $(a\gg 1)$ objects. The latter, apparently, are better connected with the boundaries of the unit volume than with each other. Conversely, the round objects are better connected with each other than with the boundaries, and therefore as the size of the system increases, $V_c(l;a)$ approaches its thermodynamic limit from above, as has been observed in various simulations for spheres under different connectivity criteria.[9,10]

The diamonds in Fig. 4 show the CFV thus obtained for systems of randomly distributed and randomly oriented interpenetrating sticks with different aspect ratios a. First, it should be mentioned that in the limit of small aspect ratios $a=l/d\ll 1$, when the sticks (Fig. 1) can be treated as spheres of diameter d, our simulations yield a CFV $\phi_c=0.29$, which is in agreement with the well established results[7,8] for soft-core spheres. This quantity is also a dimensional $(D=3)$ invariant for a system of identical interpenetrating *aligned* convex objects, including sticks, of any aspect ratio.[7–9,11] [For hard-core aligned objects, $\phi_c=0.16$ (Refs. 7 and 8)]. However, as can be seen from Fig. 4, for a system of randomly oriented sticks, the CVF is not an invariant for it drops as the aspect ratio increases. This kind of behavior can be justified in the context of excluded volume arguments[8,11] and the excluded surface/random contact model.[12] (The excluded volume, V_{ex}, is the volume around an object in which the center of an identical object should not be present if interpenetration of the two objects is to be avoided.)

In the framework of these arguments, at the threshold of percolation, the average number of bonded objects per given object (the average number of contacts per nanotube)[11]

$$B_c=N_c\langle V_{ex}\rangle, \tag{4}$$

would serve as an approximate invariant of the problem, rather than the CFV, ϕ_c. Here

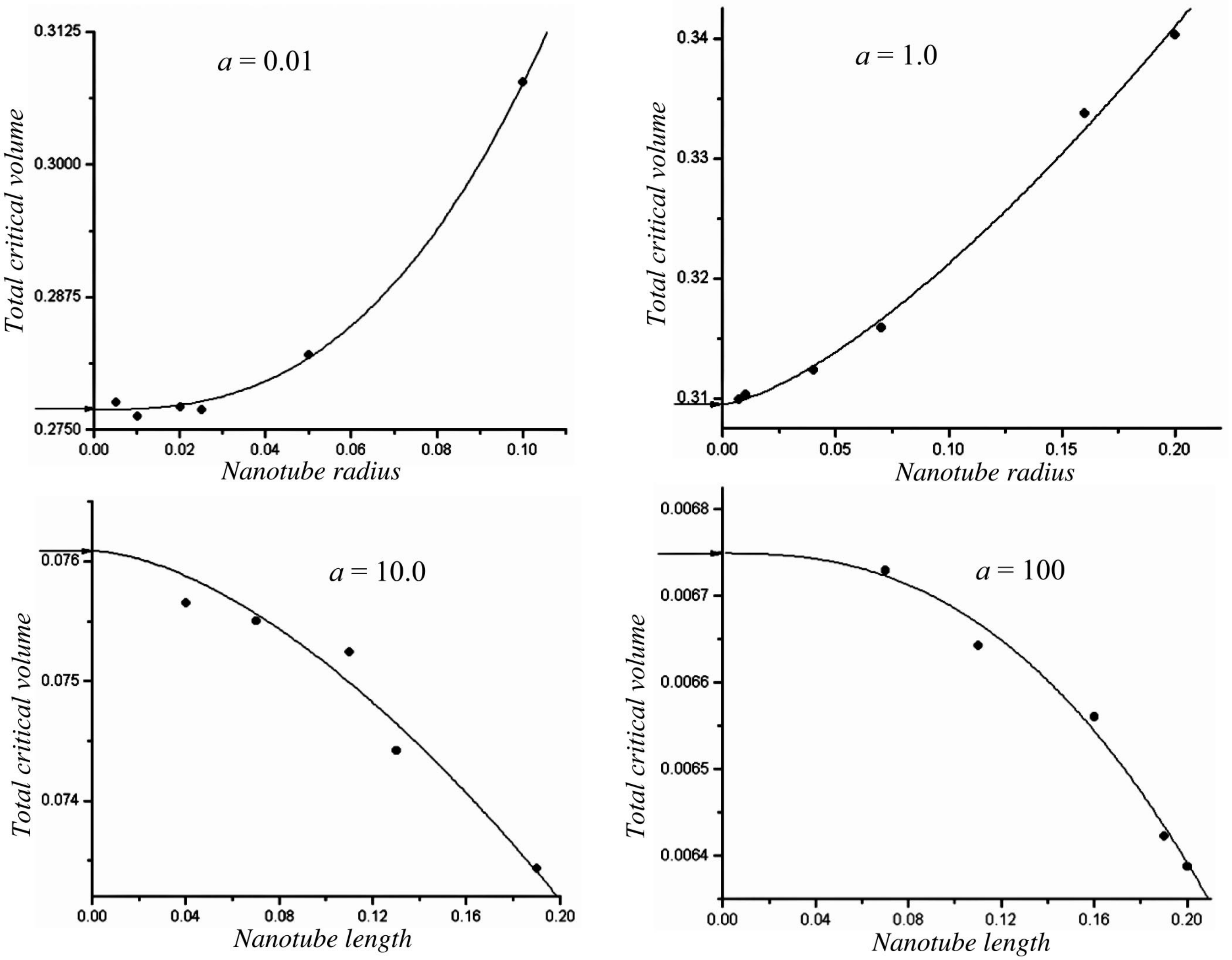

FIG. 3. Determination of the thermodynamic limit of the CFV.

$$\langle V_{ex}\rangle = 2d\left(\frac{2\pi}{3}d^2 + \pi dl + l^2\langle\sin\gamma\rangle\right) \tag{5}$$

is the excluded volume averaged over all possible mutual orientations of two sticks in contact; γ is the angle between these sticks, so that for the isotropic case $\langle\sin\gamma\rangle = \pi/4$.[11] The total critical volume, V_c, that defines the CFV in Eq. (3) can be expressed as

$$V_c(a) = B_c\frac{V}{\langle V_{ex}\rangle}, \tag{6}$$

where for the randomly oriented capped cylinders

$$\frac{\langle V_{ex}\rangle}{V} = 2\left(4 + \frac{3a^2}{2+3a}\right). \tag{7}$$

The solid curve in Fig. 4 represents the CFV (3) calculated by means of Eqs. (6) and (7) with an average number of bonds per stick equal to $B_c(a \to 0) = 2.74$, which corresponds to $\phi_c(a \to 0) = 0.29$ for the problem of soft-core spheres. It can be seen that a representation, where $B_c(a \to 0) = 2.74$ is treated as an invariant, fails to describe the simulation data at

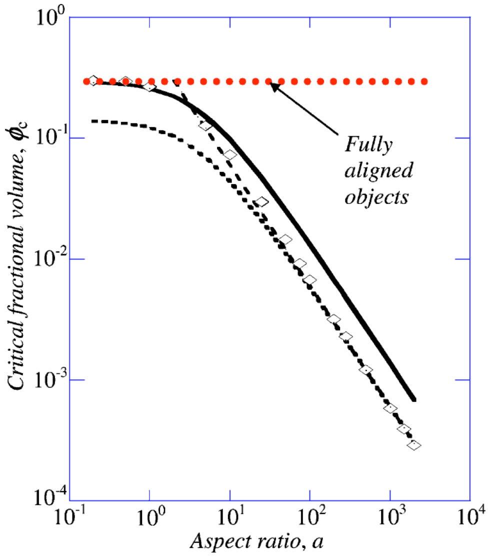

FIG. 4. Critical fractional volume for the 3D systems of randomly oriented soft-core sticks.

large aspect ratios $a \gtrsim 15$. The reason is that B_c is not a true invariant of the problem but slightly drops as a increases (see also Ref. 6). The dark dashed curve in Fig. 4 is given by Eqs. (3), (6), and (7) with $B_c(a \gg 1) = 1.20$ chosen to fit the data for large aspect ratios $a \geqslant 100$. This value of $B_c = 1.20$ is in good agreement with that established in Ref. 6 for $a \simeq 160$. Also, it is close to the $a \to \infty$ limit of $B_c = 1$ analytically predicted in Ref. 13 by a cluster expansion method.

Since $V_c(a) \ll 1$ for $a \gg 1$, then by expanding the exponent in Eq. (3) it is easy to show that for large aspect ratios the CFV is inversely proportional to a:

$$\phi_c(a \gg 1) \simeq \frac{B_c(a \gg 1)}{2a} = \frac{0.60}{a}. \tag{8}$$

The dashed straight line in Fig. 4 shows this dependence, which properly describes the data from our Monte Carlo simulations when the aspect ratio changes over several orders of magnitude.

Treating the nanotubes as soft-core (interpenetrating) objects in our simulations (shown by the diamonds in Fig. 4) ignores correlations in their spatial distribution, thus systematically overestimating the values of the CFV compared to the case of the real (hard-core) objects. However, in the limit of large aspect ratio a, also described by Eq. (3) with the average number of bonds $B_c = 1.20$, the error introduced is of the order of the ratio of the overlapping volume to the total volume of the nanotubes. This error can be shown to be of the order of $1/a$, which is less than 1% for $a \geqslant 100$. Moreover, using $B_c(a \gg 1) = 1.20$ in the interpolation formulas (3), (6), and (7) with $B_c(a \gg 1) = 1.20$ (see the dark dashed curve in Fig. 4) systematically underestimates the results of our simulations, yielding $\phi_c = 0.14$ that is fairly close to $\phi_c = 0.16$ of the hard-spheres problem.[7] One can conclude that the above interpolation formulas with $B_c(a \gg 1) = 1.20$ can be used for the evaluation of the CFV of a system of hard-core sticks of any aspect ratio.

For relatively short carbon fibers with an aspect ratio $a = 280$ dispersed in an epoxy matrix,[3,14] our simulations yield $\phi_c = 0.23\%$ in a good agreement with an experimental value of 0.25 vol. %.[14] For catalytically grown carbon nanotubes immersed in a polymer-based epoxy with a typical aspect ratio $a = 2000$, we obtained $\phi_c = 0.029\%$ as compared with 0.025–0.04 wt. % found from the data on sharp onset in the electrical conductivity of this material.[3] Also, our results do not contradict the recent data on thermal conductivity enhancement in nanotube-in-oil suspensions[1] where $\phi_c < 0.05$ vol. % for $a = 2000$ as well as in vapor-grown carbon fibers (VGCF) and single-wall nanotube (SWNT) composites[2] where $\phi_c = 1–2$ wt. % for $a = 100$ (compared to $\phi_c = 0.67\%$ that follows from our simulations) and $\phi_c = 0.1–0.2$ wt. % for $a = 1000$ (compared to the above calculated $\phi_c = 0.058\%$), respectively. Also, our calculations are in an excellent agreement with the recent experimental data[15] on electrical conductivity of the SWNT-reinforced polyimide (CP2) composites. One can conclude that, contrary to previous suggestions,[1] percolation theory can account for the surprisingly low percolation threshold observed[1–5] in carbon nanotubes suspensions and composites.

It is also clear that as the orientation of the nanotubes becomes less random, their CFV should sharply increase reaching its maximum value[7,8] of 16% for the fully aligned hard-core nanotubes of any aspect ratio. The recent data on SWNT composites[2] seem to support this conclusion. The explanation is that the disordered nanotubes form connections in the direction perpendicular to the current flow, thus promoting percolation at relatively low nanotube loadings. (For discussion, see Refs. 7 and 16)

III. DETERMINATION OF CRITICAL INDICES

Studying fluctuations of the CFV, ϕ_c, in the Monte Carlo simulations allows the critical exponent (index), t, of the conductivity problem to be found. In terms of this exponent, t, and the previously found CFV, $\phi_c(a)$, the (electro- and/or thermo-) conductivity of a nanotube suspension/composite in the vicinity of the percolation threshold can be described as the following function of the fractional volume (load), ϕ, of the nanotubes[9,17]

$$\sigma(\phi; a) = \sigma_0[\phi - \phi_c(a)]^{t(a)}, \tag{9}$$

where σ_0 is a preexponential factor that depends on the conductivity of the individual nanotubes and or of the contacts between them as well as on the topology of the percolation cluster.

To find the conductivity exponent, t, and its possible dependence on aspect ratio, a, we will start from the estimation of the critical exponent, ν, of the correlation length, L, of the percolation cluster. Being a function of the concentration, N, of the nanotubes, at the threshold of percolation the correlation length diverges as[9]

$$L \simeq l|1 - N/N_c|^{-\nu} = l|1 - \phi/\phi_c|^{-\nu}, \tag{10}$$

when $\phi \to \phi_c$. Here N_c is the critical concentration of the nanotubes and l is their length. We determined the exponent ν by studying fluctuations (variances) of the CFV $\phi_c(a)$ of 3D systems of nanotubes of a given aspect ratio, a, with consecutively decreasing length l and diameter $d = l/a$. Figure 5 gives examples of such dependencies where the following scaling law[9] (solid lines)

$$\mathrm{var}[\phi_c(a)] = Cl^{1/\nu} \tag{11}$$

has been used to find ν by means of a nonlinear fitting procedure. (Here the diamonds describe the results of our Monte Carlo simulations with each point representing the average over 100 realizations of the percolation cluster.) We found that contrary to the standard assertions,[17] the critical exponent ν is not universal: it substantially drops from 1.0 to 0.6 as the aspect ratio increases over four orders of magnitude.

We employed the scaling hypothesis (see Ref. 9 and the next section for details) to relate the critical exponents ν and t:

$$t_d = (d - 1)\nu, \tag{12}$$

where $d = 2$ or 3 is the dimensionality of the system. The diamonds in Fig. 6 show the calculated critical exponents t_3 for 3D systems consisting of identical randomly distributed

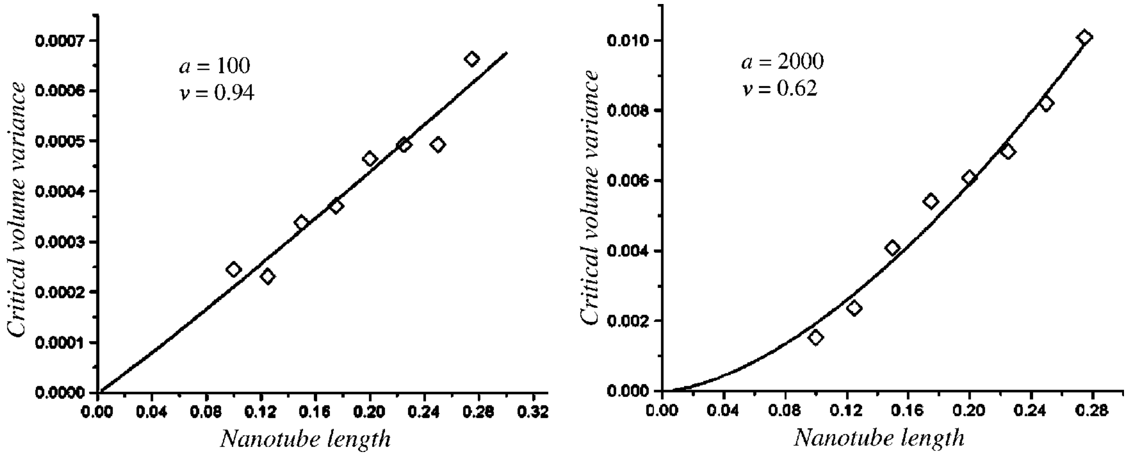

FIG. 5. Determination of the critical exponent ν of the correlation radius.

and randomly oriented spherocylinders. It can be seen that, in agreement with the previously obtained results for 3D systems of identical round objects,[17] the conductivity exponent $t_3 \simeq 2.0$ when $a \lesssim 1$. Meanwhile, for 3D systems consisting of oblong objects it is smaller than 2.0 and drops as the aspect ratio increases. In particular, for 3D systems of randomly distributed and randomly oriented nanotubes with aspect ratios of the order of $10^2 - 10^3$, the conductivity exponent $t_3 \simeq 1.2 - 1.6$, which is close to the conductivity exponent for 2D systems, where $t_2 \simeq 1.1 - 1.4$.[9,17,18] Also, the above values of $t_3 \simeq 1.2 - 1.6$ are in a good agreement with the recent experimental data on thermal[1] and electrical[4] conductivity of nanotube suspensions and composites where for the latter $t_3 = 1.36$.[4]

To verify the dependence of the conductivity exponent on the aspect ratio, we studied the statistics of the percolation clusters *above the percolation threshold*. The Monte Carlo approach allowed us to find the density of the percolation cluster, $P = N_p / N$, that is, the fraction of the nanotubes belonging to the percolation cluster, as a function of the total number of nanotubes, N, measured in the units of the critical numbers N_c at which the percolation has been achieved. This was achieved as follows. After the critical percolation cluster, which connects the opposite sides of the system is detected, the code adds new nanotubes, and determines if they are connected to the percolation cluster, or cause other clusters to be joined to the percolation cluster. The number of nanotubes N_p in the modified percolation cluster is recorded.

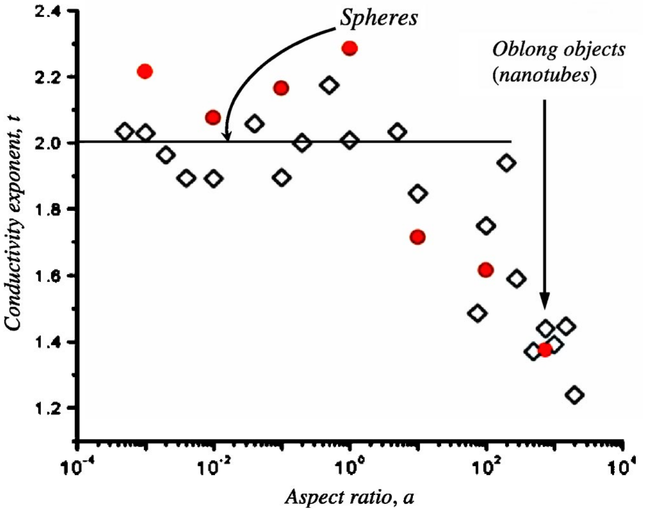

FIG. 6. Critical exponent t for 3D systems of nanotubes as a function of aspect ratio calculated by means of: (a) the scaling hypothesis Ref. 9 (diamonds) and (b) the Alexander-Orbach conjecture (Ref. 17) (circles).

Typical results of these simulations for the systems of nanotubes with different aspect ratios a are presented in Fig. 7. Here the solid lines correspond to the best fit achieved by means of the following scaling law:

$$P = C(N/N_c - 1)^{\beta}, \tag{13}$$

where β is the so called critical exponent of the density of the percolation cluster.[9,17]

We then used the Alexander-Orbach conjecture[17] which assumes that the so-called fracton or spectral dimension, d_s, which describes the number of frequency-dependent excitations on fractals, is very close to $4/3$ in all dimensions $d \geqslant 2$. It allowed us to relate the calculated exponent β and the previously found critical exponent, ν, of the correlation length L [Eq. (10)] with the exponent t_d of the conductivity problem:

$$t_d = \frac{1}{2}[(3d - 4)\nu - \beta], \tag{14}$$

where $d = 2$ or 3 is the dimensionality of the system. Figure 5 shows the calculated exponent t_3 (the circles) as a function of a. It can be seen that both the scaling hypothesis (12) and the Alexander-Orbach conjecture (14) yield quite similar results, namely, that for 3D systems, the conductivity exponent substantially decreases with the increase of the aspect ratio of the fillers.

IV. ESTIMATION OF THE PREEXPONENTIAL FACTOR

According to the scaling hypothesis,[9] the topology of the percolation cluster is determined only by its correlation length L. This conjecture allows one not only to relate the

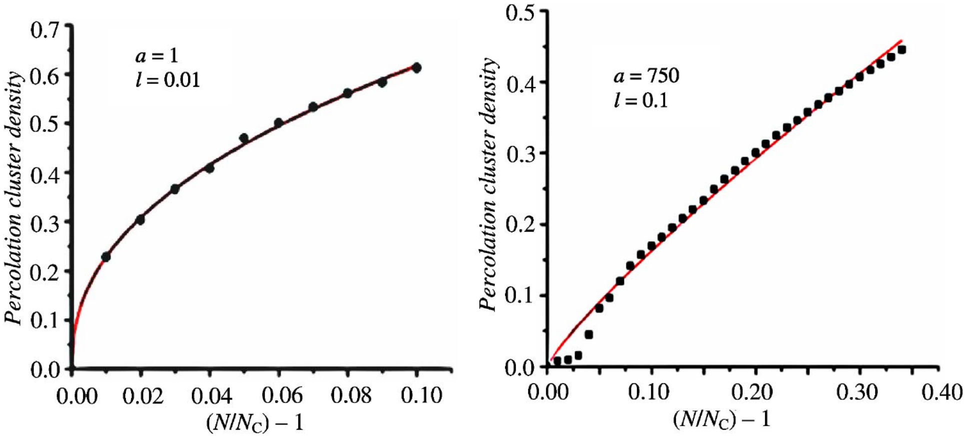

FIG. 7. The density of the percolation cluster, P, as a function of nanotube loading. For $a=1$, the exponent $\beta=0.43$; for $a=750$, $\beta=0.85$.

critical exponents of the correlation radius and of the conductivity problem but also to estimate the preexponential factor in Eq. (9). Suppose R_0 is the resistance of the nanotube or of the contact between the nanotubes, whichever is larger, and l is the length of the nanotube (or the typical distance between the contacts in question). Then the resistance of a "macrobond," whose length is of the order of the correlation length, is $R\simeq R_0 L/l$. On a scale greater than L, the percolation cluster is homogeneous. Therefore, its conductivity is of the order of a cube (square) with a side equal to L, i.e., $\sigma \simeq 1/(RL^{d-2})$. Then from Eq. (10) it immediately follows that

$$\sigma \simeq \frac{|1-\phi/\phi_c|^{(d-1)\nu}}{R_0 l^{d-2}} = \sigma_0 |\phi - \phi_c|^{t_d}. \qquad (15)$$

This proves the validity of Eq. (12) and shows that for 3D systems the preexponential factor in Eq. (9) can be estimated as

$$\sigma_0 \simeq (R_0 l \phi_c^{t_3})^{-1}. \qquad (16)$$

Let us assume, for a moment, that for sufficiently long nanotubes, their resistance exceeds that of a contact between them. (It may not be the case when the contact resistance is very large, as will be demonstrated in the next section for electrical conductivity of carbon nanotube composites.) Then by means of Eqs. (16) and (8) it is easy to show that

$$\sigma_0 \simeq \sigma_{nt}/a^{2-t_3}, \qquad (17)$$

where σ_{nt} is the conductivity of a nanotube. From here the following important conclusion can be drawn, subject to the above assumption: even at relatively large loads $\phi\simeq 1$, the conductivity of a system of nanotubes of large aspect ratio $a \gg 1$ will be much smaller than that of the individual nanotubes. Therefore, one cannot take experimental data on $\sigma(\phi)$, usually obtained for small nanotube loads ($\phi \ll 1$), and extrapolate them to $\phi \to 1$ in order to estimate the conductivity of the individual nanotubes even when the resistivity of the network is fully determined by the resistance of the nanotubes.

Also, from Eqs. (9) and (17) it follows that as the aspect ratio a increases, the preexponential factor in the expression for conductivity decreases while the exponential term increases, because above the percolation threshold $\phi_c \ll \phi < 1$ and $t(a)$, which is greater than unity, decreases. As a result, there is an optimal point where the conductivity of the nanotube suspension/composite reaches a maximum as a function of the aspect ratio, a, given that the resistivity of the nanotubes exceeds that of the contacts between them. The analysis of the experimental data available, which is presented in the next section, shows that this may be the case for thermal conductivity in nanotube-in-oil suspensions.

V. ELECTRICAL AND THERMAL CONDUCTIVITY: THEORY VERSUS EXPERMENT

We have used Eqs. (9) and (16) combined with our calculations of $t_3(a)$ and the CFV to analyze the experimental data on electrical and thermal conductivity of the nanotube suspensions and composites. It allowed us not only to explain the nonlinear dependence of the conductivity on the nanotube loading, but also to draw certain conclusions on the nature of the percolation clusters responsible for the transport properties of these materials. In brief, our findings can be summarized as follows.

A. Thermal conductivity

The filled circles in Fig. 8 represent the experimental data[1] on the thermal conductivity of multiwalled carbon nanotubes (MWNT's) of mean diameter of 25 nm and length 50 μm (with an average aspect ratio $a=2000$) dispersed into a synthetic poly (α-olefin) oil of very low thermal conductivity $\sigma_{oil}=0.1448$ W/mK. It can be seen that the addition of a very small quantity of nanotubes produces a remarkable enhancement of the effective thermal conductivity, σ, of the suspension. Using the previously calculated CFV, $\phi_c(a)$ (Fig. 4), and the conductivity exponent, $t(a)$ (Fig. 6), we estimated a CVF $\phi_c=0.00030$ or 0.03% and a conductivity exponent $t=1.24$ for the system in question. Then we used Eq. (9) to fit (see Fig. 8, the dotted line) the experimental data with one free parameter $\sigma_0/\sigma_{oil}=445$. [Using $t=1.40$ as an additional free parameter (the solid line) yields $\sigma_0/\sigma_{oil}=944$, which does not substantially improve the agreement between the theory and experiment.] As a result, the preexponential factor in Eq. (9) can be estimated as $\sigma_0=64$–137 W/mK. Then Eq. (16) yields the thermal resistance of the nanotube or of the contact between the nanotubes, whichever is greater, to be of the order of $R_0=10^7$–10^8 K/W. This is in good agreement

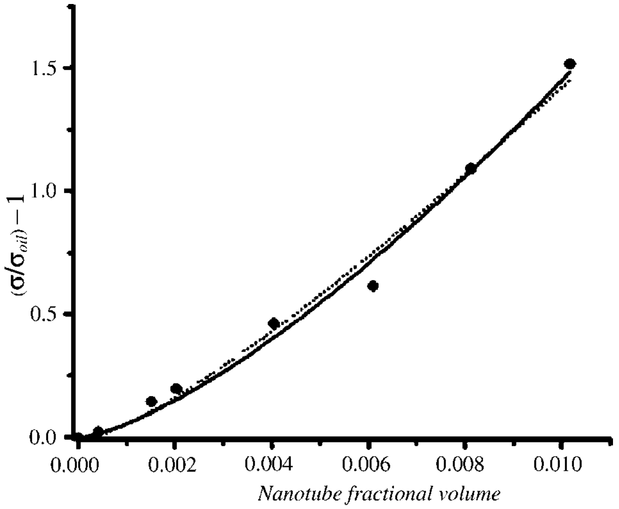

FIG. 8. Thermal conductivity of the nanotube-in-oil suspensions (measured in units of the conductivity of oil): experiment (Ref. 1) vs theory.

with the thermal resistance of an individual MWNT, $R_{nt} = 3.4\times 10^{7}$ K/W, estimated using an experimental room-temperature value of $\sigma_{nt}=3000$ W/mK for its thermal conductivity[19] if one takes $d=25$ nm and $l=50$ μm. So, one can conclude that, contrary to conventional effective medium models,[1] the percolation theory approach gives a quite accurate quantitative description of the thermal conductivity of nanotube-in-oil suspensions.

B. Electrical conductivity

The same procedure has been employed to compare the predictions of our theory with recent experimental data on the electrical conductivity of a SWNT-reinforced CP2 composites.[5] These composites were synthesized by *in situ* polymerization of monomers of interest in the presence of sonication. This process enabled uniform dispersion of SWNT bundles in the polymer matrix.[5] The experimental conductivity (Fig. 9, filled circles) was found to obey a percolationlike power law (9) with a relatively low percolation threshold loading $\phi_c=0.0005$, or 0.05%. (This allowed us to estimate the aspect ratio, a, to be close to 1200 which is consistent with the results of transmission electron microscopy measurements.[5]) Then we employed the calculated dependence $t(a)$ (Fig. 6), which gave us $t=1.43$. And finally, we used $\sigma_0=7.7\times 10^{-4}$ S/cm to obtain the best fit (Fig. 9, the dotted curve) with the experimental data. (The solid curve represents the best fit obtained by means of the two free parameters: $t=1.60$ and $\sigma_0=1.6\times 10^{-3}$ S/cm.) Based on these values of σ_0, t, ϕ_c, and $l\simeq 10^{-6}$ m, Eq. (16) allowed us to estimate the resistance R_0 to be of the order of 10^{13} Ω. This value is many orders of magnitude greater than the resistance, $R_{nt}\simeq 10^{4}$–10^{5} Ω, of SWNT's of comparable size.[20] Also, it substantially exceeds the 1 MΩ resistance of the SWNT/Pt contact measured in Ref. 20, as well as the rigid-contact resistance of 3.4 MΩ between two perpendicular SWNT's recently calculated in Ref. 21. This very high value of R_0 means that the electrical conductivity of the compound is controlled by a comparatively large, probably tunnel-type resistance of the contacts between the SWNTs that belong to the percolation cluster. [The authors of Ref. 4 have come to the same conclusion while studying electrical conductivity of polymer (PmPV or PVA)/carbon-nanotube composite thin films.] In future experiments, it seems natural to explore how the modification and/or functionalization of the SWNT surfaces would change the nanotube-nanotube contact resistance that dominates the electrical properties of the composites.

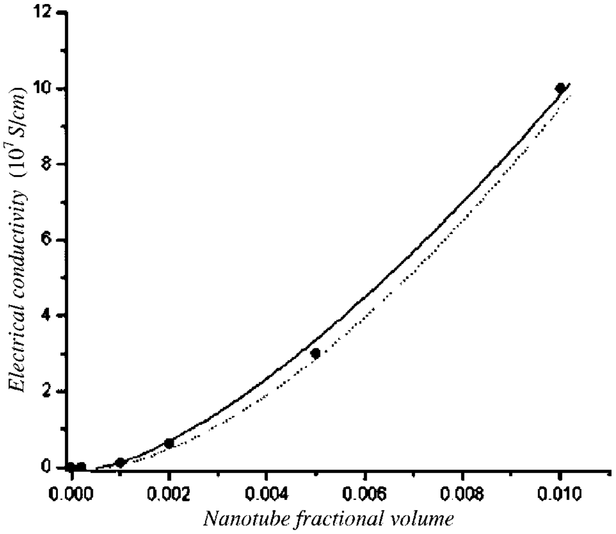

FIG. 9. Electrical conductivity of SWNT/CP2 compounds: experiment (Ref. 5) versus theory.

VI. CONCLUSIONS

The Monte Carlo simulations and the percolation theory approach we have developed successfully explain the extremely-low-threshold carbon nanotube loads that are needed to substantially enhance the conductivity of the low-conductive matrix or fluid, as well as the superlinear dependence of the conductivity of nanocomposites and nanosuspensions on the nanotube load above the percolation threshold. In addition, it allowed us to extract some important information concerning the nature of the percolating networks responsible for the transport phenomena in nanocomposites. In particular, it has been shown that (a) the thermal resistance of nanotube-in-oil suspensions above the percolation threshold is fully determined by carbon nanotubes, but (b) the electrical resistance of the SWNT/polymer compounds is governed by the extremely high resistance of the contacts between the nanotubes belonging to the backbone percolation cluster.

ACKNOWLEDGMENTS

This work has been supported by the ARL Grant No. DAAD19-02-2-0011. The authors are grateful to B. I. Shklovskii and C. Park for the valuable discussions.

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