

Monte Carlo Simulation of Nanotube Suspensions and Composites

M. Foygel*, R. D. Morris**, D. Anez*, S. French*, and V. Sobolev*

*South Dakota School of Mines and Technology, Rapid City, SD 57701, USA

**USRA/RIACS, NASA Ames Research Center, Moffett Field, CA 94035, USA

ABSTRACT

Monte Carlo simulations have been performed, aimed at finding a critical fractional volume associated with the onset of percolation for randomly oriented nanotubes dispersed in a low thermo- or electro-conductive medium. Nanotubes were treated as capped interpenetrating conductive cylinders (“sticks”) with a high (up to 2000) aspect ratio a . It has been found that for these aspect ratios critical fractional volume is inversely proportional to a resulting in a surprisingly low filler volume loadings of the order of 0.01% required to achieve percolation in such systems in a good agreement with recent experimental data on thermal and electrical conductivity of carbon nanotube suspensions and composites.

Keywords: carbon nanotube suspension, Monte Carlo

1 INTRODUCTION

Recent 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 the existing theoretical models and is nonlinear with nanotube loadings. In comparison with other nanostructured materials (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. Measurements of thermal [1,2] and electrical [2,3] conductivity of nanotube suspensions [1] and composites [2] also reveal a negligibly small percolation threshold (critical fractional volume, (CFV)) for these materials. That is why attempts to explain the conductivity of materials in question so far have been restricted to 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. In the present paper we will show that percolation theory can well account for very low conductivity thresholds in materials with conductive filler made of particles with sufficiently large aspect ratios.

2 COMPUTATIONAL PROCEDURE

A Monte Carlo simulation code has been developed and implemented. It aimed at finding a critical fractional volume (CFV) of nanotubes suspended in a low thermo- or electro-conductive medium. The code works as follows. A certain number N (smaller than the critical one) of capped cylinders (sticks) with given length l and diameter d (see Fig. 1) are randomly planted in a unit cube (both l and d are measured in the units of the unit cube size).

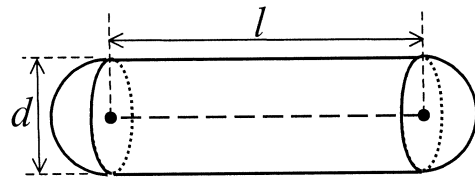


Figure 1. A capped cylinder

The centers of the mass of these sticks are given random coordinates, and two angles specifying the orientation of their axes are randomly distributed within the intervals $(0, \pi/2)$ and $(0, 2\pi)$. The sticks are considered to be interpenetrating (soft-core). 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. The code also updates (if necessary) the clusters form 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 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 $\langle \tilde{N}_c(l; a) \rangle$ averaged over different realizations of the percolation cluster.

This procedure was repeated for a given a and a successively increased size of the system or, which is equivalent, for a diminished size of l and $d = l/a$. The thermodynamic limit, $V_c = N_c v$, of a total critical volume of the occupying sticks has been evaluated by means of the following extrapolation formula:

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

Here A and λ are constants and

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

is the volume of the capped cylinder (Fig. 1). Then the critical fractional volume (CFV) can be calculated as (see Refs [4,5] for details)

$$\phi_c = 1 - \exp[-V_c(a)]. \quad (3)$$

3 MAIN RESULTS

The CFV for the different aspect ratios a , which results from the Monte Carlo simulations is presented in Fig. 2 by means of the diamonds.

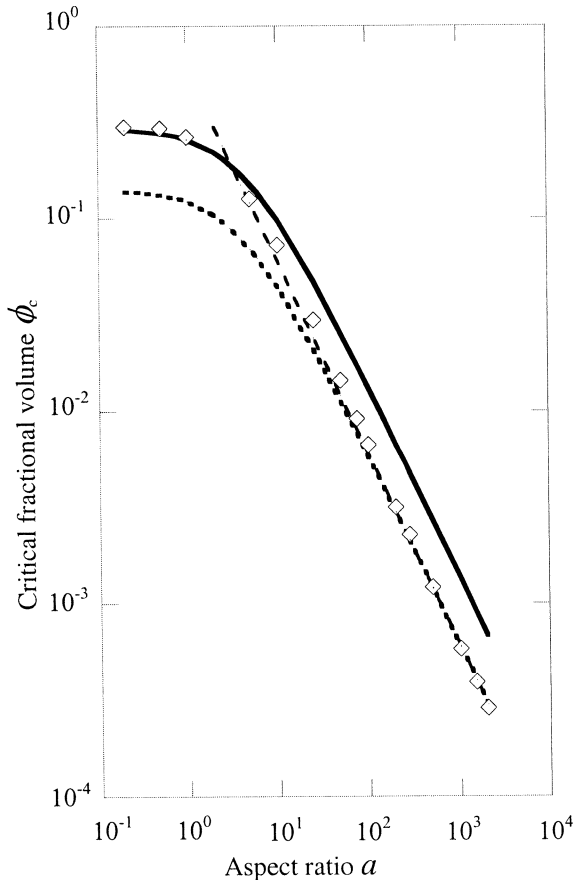


Fig. 2. Critical fractional volume for the system of randomly oriented soft-core sticks.

First of all, it should be mentioned that in the limit of extremely small aspect ratios $a = l/d \ll 1$, when the sticks (Fig. 1) can be treated as spheres of a diameter d , our simulations yield a CFV $\phi_c = 0.29$ in accordance with the well established results [4,5] for soft-core spheres. This quantity is a dimensional invariant for a system of identical interpenetrating aligned convex objects including sticks of any aspect ratio. (For hard-core aligned objects, $\phi_c = 0.16$ [4,5].) However, as can be seen from Fig. 2, for the system of randomly oriented sticks, $\phi_c(a)$ is not an invariant for it drops as aspect ratio increases. This kind of dependence can be justified in the context of the excluded volume arguments [5,6] and of the excluded surface/random contact model [7]. (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, the average number of bonded objects per given object (average number of contacts per one nanotube), [6]

$$B_c = N_c \langle v_{ex} \rangle, \quad (4)$$

rather than ϕ_c , would serve as an approximate invariant of the problem. The total critical volume, $V_c = N_c v$, that defines the CFV in Eq. (3) can be expressed as

$$V_c(a) = B_c v / \langle v_{ex} \rangle, \quad (5)$$

where for the randomly oriented capped cylinders (see Ref. [6] for details)

$$\frac{\langle v_{ex} \rangle}{v} = 2 \left(4 + \frac{3a^2}{2+3a} \right). \quad (6)$$

The solid curve in Fig. 2 represents the CFV (3) calculated by means of formulas (5) and (6) with $B_c(a \rightarrow 0) = 2.74$ corresponding to $\phi_c(a \rightarrow 0) = 0.29$ for the problem of the soft-core spheres. It can be seen that such a representation fails to describe the simulation data at large aspect ratios $a \geq 15$. The reason is that B_c is not a

true invariant of the problem but slightly drops as a increases. The dotted curve in Fig. 2 is given by Eqs (3), (5) and (6) with $B_c(a \gg 1) = 1.20$ chosen to fit the data for large aspect ratios $a \geq 100$. (In this case, the average number of bonded nanotubes is close to one, i.e. the majority of the nanotubes do not belong to the percolation cluster and are located in the “pores” of this cluster.)

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 $a \geq 50$ the CFV is inversely proportional to a :

$$\phi_c \approx \frac{B_c(a \gg 1)}{2a} = \frac{0.6}{a}. \quad (7)$$

The dashed line in Fig. 2 shows this dependence, which describes the data from the Monte Carlo simulations when the aspect ratio changes over several orders of magnitude.

Eq. (7) has been obtained for the soft-core objects. It will be held for the case of the hard-core nanotubes of large aspect ratio as well because, when these are treated as soft-core objects, double counting of the overlapping volumes is not substantial. Moreover, Eqs (3), (5) and (6) with $B_c(a \gg 1) = 1.20$ (see the dotted curve in Fig. 2) can be used for the evaluation of the CFV of the hard-core sticks of any aspect ratio because even in the limit of small a these equations yield $\phi_c = 0.14$ that is fairly close to $\phi_c = 0.16$ of the hard-spheres problem.

4 COMPARISON WITH EXPERIMENT

For relatively short carbon fibers with an aspect ratio $a = 280$ dispersed in an epoxy matrix [3,8], our simulations yield $\phi_c = 0.23\%$ in a good agreement with an experimental value of 0.25vol.% [8]. 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] with $\phi_c < 0.05\text{vol.}\%$ for $a = 2000$ as well as in vapor grown carbon fibers (VGCF) and single wall nanotube (SWNT) composites [2] with $\phi_c = 1\text{-}2\text{wt.}\%$ for $a = 100$ (compared to $\phi_c = 0.67\%$ following from our simulations) and $\phi_c = 0.1\text{-}0.2\text{wt.}\%$ for $a = 1000$ (compared to $\phi_c = 0.058\%$), respectively. One can conclude that, contrary to previous suggestions [1], percolation theory can

account for the surprisingly low percolation threshold observed [1-3] in carbon nanotubes suspensions and composites.

It is also clear that with the increase of the orientation of nanotubes their CFV should sharply increase reaching its maximum value of 16% [4,5] for 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 percolations at relatively low nanotube loadings. (For discussion see Refs [4,9].)

Research was sponsored by the Army Research Laboratory and was accomplished under Cooperative Agreement # DAAD19-02-2-0011. The views and conclusions contained in this document are those of the authors and should not be interpreted as representing the official policies, either expressed or implied, of the Army Research Laboratory or the US Government. The US Government is authorized to reproduce and distribute reprints for Government purposes notwithstanding any copyright notation hereon.

REFERENCES

- [1] S. U. S. Choi, Z. G. Zhang, W. Yu, F. E. Lockwood, and E. A. Grulke, *Appl. Phys. Lett.* **79**, 2252 (2001).
- [2] M. J. Biercuk, M. C. Llaguno, M. Radosavljevic, J. K. Hyun, A. T. Johnson, and J. E. Fisher, *Appl. Phys. Lett.* **80**, 2767 (2002).
- [3] J. Sandler, M.S. P. Shaffer, T. Prasse, W. Bauhofer, K. Schulte, and A. H. Windle, *Polimer* **40**, 5967 (1999).
- [4] G. E. Pike and C. H. Seager, *Phys. Rev. B* **10**, 1421 (1974).
- [5] I. Balberg, *Phys. Rev. B* **33**, 3618 (1986).
- [6] I. Balberg, C. H. Anderson, S. Alexander, and N. Wagner, *Phys. Rev. B* **30**, 3933 (1984).
- [7] A. P. Philipse, *Langmuir* **12**, 1127 (1996).
- [8] F. Carmona, P. Prudhon, and F. Barreau, *Solid State Commun.* **51**, 255 (1984).
- [9] I. Balberg and N. Binnema, *Phys. Rev. B* **28**, 3799 (1983).