Random walks in nanotube composites: Improved algorithms and the role of thermal boundary resistance

Hai M. Duong, Dimitrios V. Papavassiliou, Lloyd L. Lee, and Kieran J. Mullen

Citation: Appl. Phys. Lett. **87**, 013101 (2005); doi: 10.1063/1.1940737
View online: http://dx.doi.org/10.1063/1.1940737
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v87/i1
Published by the American Institute of Physics.

Random walks in nanotube composites: Improved algorithms and the role of thermal boundary resistance

Hai M. Duong, Dimitrios V. Papavassiliou,[a] and Lloyd L. Lee
School of Chemical, Biological and Materials Engineering, The University of Oklahoma, Norman, Oklahoma 73019

Kieran J. Mullen
Department of Physics and Astronomy, The University of Oklahoma, Norman, Oklahoma 73019

(Received 4 February 2005; accepted 25 April 2005; published online 27 June 2005)

Random walk simulations of thermal walkers are used to study the effect of interfacial resistance on heat flow in randomly dispersed carbon nanotube composites. The adopted algorithm effectively makes the thermal conductivity of the nanotubes themselves infinite. The probability that a walker colliding with a matrix-nanotube interface reflects back into the matrix phase or crosses into the carbon nanotube phase is determined by the thermal boundary (Kapitza) resistance. The use of "cold" and "hot" walkers produces a steady state temperature profile that allows accurate determination of the thermal conductivity. The effects of the carbon nanotube orientation, aspect ratio, volume fraction, and Kapitza resistance on the composite effective conductivity are quantified. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1940737]

The impressive physical, thermal, and electrical properties of carbon nanotubes (CN) have the potential to improve the properties of polymer composites. The thermal conductivity is estimated at 3000 W/mK for an isolated multiwall CN[1] and between 1750 and 6600 W/mK for a single wall CN (SWNT) at room temperature.[2–4] Based on the predictions of Maxwell's formula[5] or of the simple "mixture law," one would expect CN composites with low conductivity polymers (i.e., conductivity less than 0.5 W/mK) to demonstrate an effective conductivity tens of times higher than the conductivity of the polymer matrix, even for 1.0 wt % CN. However, experimental evidence has shown that the addition of up to 2.0 wt % of CNs into industrial epoxy composites increases their thermal conductivity by up to 125%.[6] Suspensions of nanotubes in oil, on the other hand, show an enhancement of the effective conductivity relative to the Maxwell predictions for spherical inclusions.[7]

It appears that the thermal resistance (or Kapitza resistance)[8–12] of the CN-matrix interface, which is not taken into account in the development of Maxwell's theory, plays a significant role in the determination of the conductivity of a composite or a suspension. The thermal resistance to heat transfer through an interface becomes important when the high conductivity inclusions are small in size, and their surface to volume ratio is high.[13] The case of CN composites falls in this category, and, Molecular Dynamics simulations[14] have shown that the thermal resistance is important for the case of CN suspensions in octane liquid.

The present work is a computational study of the thermal properties of dispersed-nanotube composites by taking into account the Kapitza resistance. An algorithm based on the random walk[15] of thermal markers in a composite matrix with dispersed cylinders is used. Tomadakis and Sotirchos[16,17] have used a similar algorithm to study the transport properties of random arrays of cylinders in a conductive matrix. In our algorithm, we treat the CN thermal conductivity as effectively infinite, obviating the need to model random walks within the nanotubes. This approximation is appropriate, since the CN conductivity is much higher than that of the matrix (e.g., three orders of magnitude for epoxy). Our algorithm is, thus, more efficient than a typical random walk algorithm, and much faster than a Molecular Dynamics algorithm. Even though it cannot provide results at the fundamental molecular level as Molecular Dynamics can, it can be used to model physicochemical properties of randomly dispersed nanotube materials quite successfully.

The computational domain for the numerical simulation is a cubic cell with two phases; one phase is the matrix and the other is the CN cylinders that are dispersed into the matrix phase. The computational cell is divided in bins, and the temperature distribution is calculated from the number of walkers in each bin. The computation of the effective transport coefficients is based on an off-lattice Monte Carlo simulation of random walkers traveling in the computational cell for a relatively long time. Heat flux is in the x direction. Heat walkers are initially distributed uniformly at the surface $x=0$, and then move with random jumps that follow a normal distribution into the computational cell. The walkers exit at the surface $x=2b$ (for a constant flux boundary condition) or bounce back into the computational cell (for an isothermal boundary condition). The cell is periodic in other directions. The displacement of the walkers in the matrix is due to Brownian motion[18] and can be described by a normal distribution with a zero mean and a standard deviation that depends on the matrix thermal diffusivity, D_m. The standard deviation of the distribution in each one of the space dimensions is $\sigma=\sqrt{2D_m\Delta t}$, where Δt is the time increment.

The following assumptions were made.

(1) The CN thermal conductivity is much greater than that of the matrix,[1–4] and therefore walkers distribute uniformly once inside the CNs.
(2) Collisions between walkers are ignored. The random walk reflects the scattering of phonons by the disordered matrix material (i.e., the interaction of the walkers with the matrix). Walker–walker interactions would reflect

[a]Electronic mail: dvpapava@ou.edu

thermal conductivity that depends on the local temperature, and we ignore such nonlinear interactions.

(3) The properties of the materials (e.g., density, specific heat, thermal relaxation length) do not change with temperature over the range modeled.

(4) The thermal resistance for a heat walker traveling from the matrix to a CN equals that from a CN to the matrix, as required by the principle of microscopic reversibility.

(5) The product of the CN density and heat capacity equals that of the matrix, so that in thermal equilibrium the walker density would be uniform inside and out of the CNs.

(6) All walkers bounce back when they reach the surface $x=0$, so that they cannot enter and immediately leave. This allows us to fix the heat flux at that surface.

With the earlier assumptions, once a walker in the matrix reaches the interface between the matrix and a CN, the walker will move into the CN phase with a probability $f_{m\text{-CN}}$, which represents the thermal resistance of the interface (and will stay at the previous position in the matrix with a probability $1\text{-}f_{m\text{-CN}}$). Similarly, once a walker is inside a CN, the walker will redistribute randomly within the CN with a probability $(1\text{-}f_{\text{CN-}m})$ at the end of a time step, and will cross into the matrix phase with a probability $f_{m\text{-CN}}$. In this later case, the walker moves first to a random point anywhere on the surface of the CN and then moves with a normal distribution into the matrix.

According to assumption (4) earlier, the thermal resistance is the same when a walker moves from one phase into the other, but this does *not* mean that $f_{m\text{-CN}}=f_{\text{CN-}m}$. To see why, we consider the case of a slab of material with a large thermal conductivity embedded in the matrix. In thermal equilibrium, the average walker density within the slab should equal that in the matrix. However, if we take $f_{m\text{-CN}}=f_{\text{CN-}m}$, this will not be the case for our algorithm where walkers can leave anywhere on the surface the next time step. We must weight the exit probability $f_{\text{CN-}m}$, so that the flux of walkers into the slab equals that going out when we are in equilibrium. The weight factor depends only upon geometry, since its goal is to achieve the correct density. Careful analysis shows that to maintain equilibrium the two probabilities are related as $f_{\text{CN-}m}=(C_0\sigma A_c/V_c)f_{m\text{-CN}}$, where A_c and V_c are the surface area and the volume of a nanotube, respectively. The constant C_0 is shape and size dependent, and was set equal to unity in this work. According to the acoustic mismatch theory,[19] the average probability for transmission of phonons across the interface into the dispersion, $f_{m\text{-CN}}$, is given by $f_{m\text{-CN}}=4/\rho C C_m R_{\text{bd}}$, where ρ is the matrix density, C is the matrix specific heat, C_m is the velocity of sound in the matrix, and R_{bd} is the thermal boundary resistance.

Considering the computational time needed for each simulation and the computational errors involved, it was decided to use 90 000 walkers, a time increment of 0.25 and 128^3 bins for the rest of the simulations.

Randomly dispersed nanotube composites. The heat flow was studied in a 10 μm size cubic cell containing 0.35 μm diameter nanotubes (these quantities are scaled). The CNs were perpendicular or parallel to the direction of heat flow (i.e., the x axis), or they were randomly oriented; in all cases the location of the CNs was random. The number of CNs in the cubic cell varied from 10 to 640 and depended on the aspect ratio of the cylindrical CNs and the volume fraction of CNs. The simulations were conducted with three different orientations of CNs dispersed in composites (parallel to x axis, parallel to z axis, and random), with different thermal resistance ($f_{m\text{-CN}}=1.00$, 0.50, 0.20, 0.02) and with different volume fraction of CNs (8%, 4%, and 1%). In order to make the calculation of the effective conductivity easy, we studied heat transfer with constant heat flux through the domain with hot and cold planes at $x=0$ and $x=2b$, respectively. This was done by having "hot" walkers enter at $x=0$ and "cold" walkers (carrying negative energy)[21] enter at $x=2b$. The theoretical solution of this problem at steady state is a linear temperature profile whose slope is inversely proportional to the medium conductivity. This time-independent result was robust and trivial to fit, in contrast with the changing exponential profiles of a time-dependent problem. The simulation results for the effective thermal conductivities of dispersed-nanotube composites with constant heat flux are summarized in Table I. For each entry, the thermal conductivity was the average of three simulation runs with different initial nanotube random distributions. The matrix thermal conductivity used for the simulations was 1.0 W/mK. Figure 1 shows the thermal conductivities of nanotubes dispersed without fixed orientation in the composite (case 3 in Table I) where the ratio of the nanotube length, L, over the nanotube diameter, D, is 3.75. When either the volume fraction of the nanotubes increases or the thermal resistance decreases, walkers move from the matrix into the CN easier. In addition, the walkers can move much faster inside a CN than in the matrix due to its high thermal conduction. Hence, the effective thermal conductivity increases. Table I shows that the above trend can be observed for all three cases of dispersion pattern of CNs.

With the same thermal resistance, volume fraction and dispersion pattern of CNs, the random jump of walkers in the heat flow direction is less for case 1, higher for case 2, and maximum for case 3. This allows the heat walkers to diffuse faster in the cell. Therefore, the thermal conductivity increases in cases 1, 2, and 3, as expected.

When we change the aspect ratio of the CNs, the thermal conductivity for case 1 is not affected at a given volume fraction of nanotubes. The reason is that the random jump of walkers inside the nanotubes in the heat flow direction does

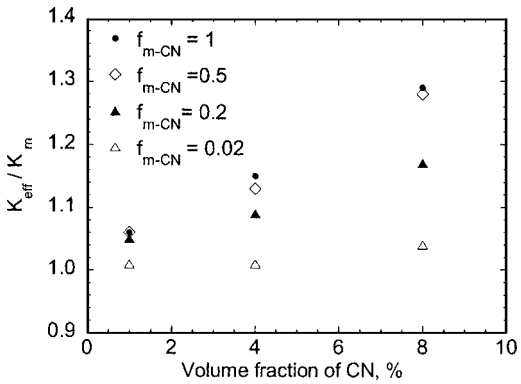

FIG. 1. Effective thermal conductivities of randomly dispersed nanotube composites as a function of the volume fraction of nanotubes at $L/D=3.75$. For each value of thermal resistance and volume fraction of nanotubes, the thermal conductivity is the average of three simulation runs with different initial nanotube random distributions.

TABLE I. Thermal conductivities of nanotube composites with constant heat flux.

		Volume fraction (%)								
		8	4	1	8	4	1	8	4	1
$f_{m\text{-CN}}$	$R_{bd}\times 10^7$(Km^2 W^{-1})[a]	L/D=3.75			L/D=7.50			L/D=15.0		
		Vertically dispersed nanotube composites (Case 1)								
1.00	0.012	1.19	1.10	1.05	1.15	1.09	1.05	1.13	1.10	1.04
0.50	0.024	1.11	1.06	1.04	1.11	1.06	1.03	1.09	1.07	1.03
0.20	0.061	1.04	1.04	1.03	1.03	1.03	1.03	1.03	1.03	1.03
0.02	0.610	1.04	1.00	0.97	1.02	0.99	0.96	1.02	1.00	0.97
		Horizontally dispersed nanotube composites (Case 2)								
1.00	0.012	1.65	1.31	1.10	2.84	2.04	1.31	3.85	2.67	1.46
0.50	0.024	1.53	1.27	1.10	2.59	1.90	1.27	3.55	2.52	1.42
0.20	0.061	1.30	1.16	1.07	1.97	1.58	1.19	2.69	2.03	1.31
0.02	0.610	1.05	1.03	1.03	1.14	1.10	1.06	1.31	1.22	1.11
		Randomly dispersed nanotube composites (Case 3)								
1.00	0.012	1.29	1.15	1.06	1.88	1.35	1.10	2.05	1.40	1.15
0.50	0.024	1.28	1.13	1.06	1.84	1.35	1.09	2.04	1.40	1.12
0.20	0.061	1.17	1.09	1.05	1.56	1.25	1.08	1.72	1.28	1.11
0.02	0.610	1.04	1.01	1.01	1.06	1.04	1.03	1.08	1.07	1.06

[a]This work is a parametric study. However, to acquire a physical sense, we apply the simulation to composites of carbon nanotubes in an epoxy resin matrix. The Kapitza resistance can be obtained from the expression given in the text. We use the approximate values: density of resin, ρ=1060 kg/m^3 (see Ref. 22), heat capacity, C=1.96 kJ/(kg K) (see Ref. 22), the velocity of sound, C_m=2400 m/s (see Ref. 23) in epoxy.

not change because nanotubes have the same diameter. However, the thermal conductivity increased highly for cases 2 and 3, as expected. When the nanotube axes are parallel to the heat flow, the nanotube length allows the walkers to travel faster in the cell. We can also conclude that the effective thermal conductivity, K_{eff}, is much lower than that calculated from the modified Maxwell theory for nonspherical inclusions, even in the case of heat transfer with cylinders oriented parallel to the direction of heat transfer.[5] The thermal conductivity of 1% volume fraction of SWNTs (K_{CN} in the range 1750–6600 W/mK) dispersed parallel to the direction of heat flow in a material with K_m=1 W/mK can be calculated to be between 18.49 and 66.99 W/mK, while the thermal conductivity obtained from the simulation results is less than 1.46 W/mK. This level of conductivity enhancement is comparable to experimental data for the thermal conductivity of nanotube composites.[1,6] For example, the thermal conductivity of 1 wt % unpurified SWNTs dispersed in industrial epoxy increased only from 0.2 to 0.29 W/mK.[6]

Conclusions. The effective thermal conductivities of nanotubes dispersed in a continuous matrix were computed over a wide range of thermal resistance, CN volume fraction, and nanotube aspect ratio. A random walk algorithm was used to simulate heat transfer through such a material under different boundary conditions and after taking into account the effects of thermal resistance. The algorithm was efficient in that it removed the need to perform random walks within the CNs. It was found that the effective thermal conductivities of nanotube composites are much lower than those calculated from the modified Maxwell theory. The effect of the Kapitza resistance becomes important when the surface area of the CNs and their aspect ratios are small.

This work was supported by the National Science Foundation, EPS-0132534. H.M.D. and D.V.P. acknowledge the Donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research through Grant PRF No. 39455-AC9, and L.L.L. acknowledges support from the National Science Foundation (CTS 0114123, and CISE/EIA 0203481). The authors also thank the National Center for Supercomputing Applications for providing supercomputer time for the computations reported here.

[1]E. S. Choi, J. S. Brooks, and D. L. Eaton, J. Appl. Phys. **94**, 6034 (2003).
[2]J. Che, T. Cagin, and W. A. Goddard III, Nanotechnology (2003).
[3]J. Hone, B. Batlogg, Z. Benes, A. T. Johnson, and J. E. Fischer, Science **289**, 1730 (2000).
[4]S. Berber, Y. K. Kwon, and D. Tomanek, Phys. Rev. Lett. **84**, 4613 (2000).
[5]R. B. Bird, W. S. Stewart, and E. N. Lightfoot, *Transport Phenomena*, 2nd ed. (Wiley, New York, 2002), pp. 282, 376 and 397.
[6]M. J. Biercuk, M. C. Llaguno, M. Radosavljevic, J. K. Hyun, and A. T. Johnson, Appl. Phys. Lett. **80**, 2767 (2002).
[7]S. U. S. Choi, Z. G. Zhang, W. Yu, F. E. Lockwood, and E. A. Grulke, Appl. Phys. Lett. **79**, 2252 (2001).
[8]P. L. Kapitza, J. Phys. (USSR) **4**, 181 (1941).
[9]A. Maiti, G. D. Mahan, and S. T. Pantelides, Solid State Commun. **102**, 517 (1997).
[10]S. Shenogin, L. Xue, R. Ozisik, P. Keblinski, and D. G. Cahill, J. Appl. Phys. **95**, 8136 (2003).
[11]J. L. Barrat and F. Chiaruttini, Mol. Phys. **101**, 1605 (2003).
[12]C. J. Twu and J. R. Ho, Phys. Rev. B **67**, 205422 (2003).
[13]A. G. Every, Y. Tzou, D. P. H. Hasselman, and R. Raj, Metall. Mater. **40**, 123 (1992).
[14]S. Shenogin, L. Xue, R. Ozisik, P. Keblinski, and D. G. Cahill, J. Appl. Phys. **95**, 8136 (2004).
[15]S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943).
[16]M. M. Tomadakis and S. V. Sotirchos, J. Chem. Phys. **98**, 616 (1992).
[17]M. M. Tomadakis and S. V. Sotirchos, J. Chem. Phys. **104**, 6893 (1996).
[18]A. Einstein, Ann. d. Phys. **17**, 549 (1905).
[19]E. T. Swartz and R. O. Pohl, Rev. Mod. Phys. **61**, 605 (1989).
[20]H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, 2nd ed. (Oxford University Press, New York, 1959), p. 97.
[21]D. V. Papavassiliou and T. J. Hanratty, Int. J. Heat Mass Transfer **40**, 1303 (1997).
[22]B. Sundqvist, O. Sandberg, and G. Backstrom, J. Phys. D **10**, 1397 (1977).
[23]A. Bick and T. Dorfmueller, NATO ASI Ser., Ser. C **291**, 389 (1989).