EFFECT OF CARBON NANOTUBE INTERFACIAL GEOMETRY ON THERMAL TRANSPORT IN SOLID-LIQUID PHASE CHANGE MATERIALS

Ronald J Warzoha^a and Amy S Fleischer^{b,*1}

^aDepartment of Mechanical Engineering, United States Naval Academy, Annapolis, MD 21402

^bDepartment of Mechanical Engineering, Villanova University, Villanova, PA 19085

Abstract

For nearly two decades, research groups have attempted to increase the thermal conductivity of bulk materials by saturating them with different concentrations and types of nanoparticles. However, optimal enhancements in the thermal conductivity of these materials continue to go unrealized, primarily due to interfacial phenomena that impede phonon propagation from the bulk material to the nanoparticle or between individual, contacting nanoparticles. Though it is almost certain that interfacial resistances between contacting nanoparticles are responsible for the underwhelming thermal performance of nanoparticles in bulk materials, the physical mechanisms that limit thermal transport at nanoparticle junctions is not well understood. In this study, we investigate the effect of nanoparticle constriction size (i.e. the contact area between linked nanoparticles) on the bulk thermal conductivity of a surrounding paraffin-based phase change material. To this end, we measure the effective thermal conductivity of different Multi-walled Carbon Nanotube (MWCNT)/paraffin nanocomposites is measured with the transient plane source technique. Using a newly developed physical model, the interfacial thermal resistance between the contacting nanoparticles is determined as a function of the constriction geometry. Results suggest that the thermal conductance (i.e. the rate of heat transfer) between contacting MWCNTs can be increased by a factor of 27 by increasing their diameter by only 58 nm. This is in direct conflict with effective medium approximations, which predict an increase in the bulk thermal conductivity of MWCNT-PCM composites when MWCNT diameters are reduced. Such a result indicates that the contact area between individual, contacting nanoparticles has a significant impact on thermal transport within the PCM nanocomposite, and therefore its bulk thermal conductivity. It is expected that these results will strongly impact the design of nanoparticle-laden PCMs.

¹ Corresponding Author, e-mail: amy.fleischer@villanova.edu

Key Words: Phase change materials; multi-walled carbon nanotubes; phonon; thermal conductivity; constriction resistance; thermal boundary conductance

Introduction

Organic phase change materials (PCMs) have the ability to remove and store heat passively, thereby making them excellent candidates for the thermal management of portable electronic devices [1] and electric vehicle batteries [2], as well as for storing and reusing thermal energy in residential solar-thermal and HVAC systems [3]–[5]. The amount of heat that can be stored within a PCM is governed by its phase change enthalpy, which is typically high for commercial paraffin waxes (on the order of 200 kJ/kg [6], [7]). As a result of their high phase change enthalpies, the amount of heat that can be stored in paraffins on a per unit mass basis is expected to be sufficient for meeting the performance expectations of the aforementioned applications.

Unfortunately, paraffin-based PCMs have exceptionally low thermal conductivities (on the order of 0.1 W/mK [8]). This is over four orders of magnitude lower than the thermal conductivity of conventional heat transfer materials (oxygen-free copper, for instance, has a thermal conductivity of ~400 W/mK [9]). The poor thermal conductivities of organic PCMs result in extremely slow melt and solidification rates and thus very little utilization of the PCM mass in thermal energy storage applications [6], [7], [10]. Low PCM thermal conductivities can also result in severe thermal gradients in close proximity to sensitive electronics and thus failure of the primary electronic component(s) in critical energy infrastructure. Consequently, it is imperative that the thermal conductivity of organic PCMs be increased.

In this work, multi-walled carbon nanotubes (MWCNTs) are inserted into an organic paraffin PCM in order to improve its bulk thermal conductivity. MWCNTs are known to have remarkably high intrinsic thermal conductivities (as high as 6,000 W/mK [11]), low densities and high surface area-to-volume ratios, making them excellent candidates for PCM thermal enhancement in applications with weight and volume constraints. Additionally, the thermal conductivity of MWCNTs can be nearly an order of magnitude greater than some of the conventional materials used in thermal management systems, primarily due to the strong sp^2 bonds that are formed between neighboring carbon atoms and the long mean free path of phonons within the nanoparticle itself [12], [13] (~1 μm for CNTs and graphene [14]).

However, the incorporation of nanoparticles into PCMs for thermal augmentation is not straightforward. This is primarily due to the fact that standard effective medium approximations often over predict the thermal conductivity of nanocomposite materials. Instead, the thermal conductivity enhancement of a nanocomposite is generally inhibited by a thermal resistance that occurs across nanoparticle interfaces [15]. This thermal resistance is governed by a variety of geometric, physical and chemical phenomena that occur at the nanoparticle-nanoparticle junction(s), and can be substantial when the nanoparticles have rough surfaces or extend in multiple dimensions [14] (as high as 10^{-4} m²K/W for carbon nanofibers, for instance [6]). On the other hand, recent molecular dynamics simulations suggest that the presence of carbon-based nanoparticles with ‘smooth’ surfaces (such as CNTs and graphene) results in the alignment of alkane molecules across carbon nanoparticle-paraffin interfaces. In turn, a significant reduction in the interfacial thermal resistance at this type of interface can be achieved [16]. Consequently, the use of carbon-based nanoparticles for enhancing the thermal conductivity a paraffin-based PCM offers the most promising method for their thermal conductivity enhancement to date.

Several groups have decreased the thermal resistance at nanoparticle-nanoparticle junctions by increasing the adhesion energy across contacting interfaces. This technique generally results in mechanically strong, percolating networks [17]–[20]. In these studies, assortments of chemical modifications are made at the nanoparticle junction(s) in order to achieve higher rates of thermal transport and increased mechanical stability. However, it is not known whether the thermal conductivity of these percolating nanocomposite PCMs can be further tuned by adjusting the size of the constriction at the interface. Preliminary molecular dynamics simulations suggest that the size of the constriction does affect thermal transport at an individual nanoparticle-nanoparticle junction [21], [22], but the range of nanoparticle sizes used for these predictions is too small to make accurate estimations about its influence on both nano-scale and macro-scale thermal transport within PCMs. Additionally, it is unknown to what degree ballistic and diffusive transport affect heat flow rates at these junctions. As a result, additional work is needed to determine the effect of nanoparticle contact area on the thermal performance and associated nano-scale and macro-scale thermal characteristics of nanocomposite PCMs.

In this study, four different MWCNTs with varying diameters and lengths are embedded within an organic paraffin PCM at concentrations above and below the percolation threshold. The objectives of this study are to determine the effect of CNT contact area on: (1) the interfacial

thermal resistance between a CNT and another CNT and (2) the ballistic and diffusive components of heat transfer on heat flow at the interface. The effective interfacial thermal resistance between two linked CNTs is calculated by saturating the PCM with different volume concentrations of CNTs and applying the effective medium model for thermal conductivity of networked composites developed by Foygel et al. [23]. The procedure for this method is described in [15]. The insight gained from this study will allow for the design of nanocomposite PCMs with tunable thermal conductivity. In this case, thermal engineers will be able to tune the thermal properties of disordered, bulk materials based on the phonon physics that occur at sub-micron CNT interfaces. Such insight will allow for the thermal optimization of next-generation CNT-based composite materials.

Experimental and Analytical Methods

Physical Properties of Materials

The geometric properties for each of the different nanoparticles that are used in this study are listed in Table 1. In total, four different types of CNTs are used to produce the nanocomposites for this work. The values for the diameter, length and density of the nanoparticles are obtained from the manufacturer (US Research Nanomaterials, Inc.).

v	Density (kg/m ³)	Diameter (nm)	Length (μm)	Aspect Ratio	Φ _c (%)	A _o (nm ²)
1	2100	7	20	2857.0	0.022	270
2	2100	10	50	5000.0	0.012	587
3	2100	25	15	800.0	0.078	2390
4	2100	65	15	230.8	0.269	16500

Table 1: MWCNT physical properties

In Table 1, Φ_c is the volume fraction at which the nanoparticles begin to percolate and A_o is the average overlap area between nanoparticles (which is distinctly different from contact area, mentioned later). Eqn. 1, developed by Foygel et al. [23] (and later confirmed by Wemhoff [24]), is used to determine Φ_c.

$$\phi_c = \frac{0.6}{p} \quad (1)$$

In Eqn. 1, p represents the aspect ratio of the nanoparticle. The average overlap area between nanoparticles can be calculated according to Wemhoff [24] and is determined using Eqn. 2.

$$A_o = \frac{2D^2}{\pi} \zeta(p) \quad (2)$$

where,

$$\zeta(p) = \ln \left[\frac{\sqrt{1+p^{-1}} + \sqrt{1-p^{-1}}}{\sqrt{1+p^{-1}} - \sqrt{1-p^{-1}}} \right] \quad (3)$$

In Eqns. 2 and 3, D is the diameter of the nanotube, and p is the aspect ratio of the nanoparticle ($p = L/D$, where L is the length of the nanoparticle).

The thermophysical properties of the commercial paraffin (IGI 1230A) used in this work are listed in Table 2 and are supplied by the manufacturer.

Thermal Conductivity (W/mK)	Density (kg/m ³)	Specific Heat (J/kgK)	Thermal Diffusivity (mm ² /s)	Melt Temperature (K)	Phase Change Enthalpy (kJ/kg)
0.25	880	2100	0.14	329.15	290

Table 2: Thermophysical properties of IGI 1230A paraffin wax at 300 K

Materials Fabrication

Randomly oriented MWCNT/paraffin nanocomposites are synthesized using a two-step technique. MWCNTs are first embedded within a melted paraffin wax ($T_{\text{melt}} = 329.15$ K) at concentrations ranging from 0.003 v% to 5 v% and are subsequently dispersed using a sonic horn. For dispersion, the ultrasonic horn is pulsed continuously at 32 Hz for 20 minutes. The resulting liquid paraffin composite material is poured into two separate cylindrical molds (diameter = 2.8 cm, height = 1.4 cm) that rest on a polished stainless steel substrate. The mirror finish on the stainless steel substrate is designed to minimize the surface roughness of the face of the solid composite that directly touches the Transient Plane Source sensor in order to minimize the thermal interface resistance between the sensor and the surrounding material (it should be noted, though, that this effect can be eliminated by adjusting the starting time for the Transient

Plane Source curve fit procedure, which is described briefly in the next section and in detail in other work [25], [26]).

Thermal Conductivity Measurements

The thermal conductivity of each MWCNT/paraffin nanocomposite is measured using a Transient Plane Source (TPS) device. The details of this measurement technique and its use for measuring the thermal conductivity of nanocomposites are described elsewhere [26]. For this technique, a double-spiral nickel foil sensor is used to both direct heat into a surrounding material and measure the temperature within the foil. The transient temperature distribution within the foil is obtained using a Wheatstone bridge and is related to the temperature rise in a surrounding material as a function of the applied heat flux at the sensor interface. For solid samples, the sensor is sandwiched between each material, while for liquid samples the sensor is immersed within the material. Theoretically, a large temperature rise per unit time corresponds to a more thermally insulating material, whereas a small transient temperature rise indicates that the material behaves as a thermal conductor.

A number of different physical phenomena are known to affect the accuracy of this measurement technique. First, it is critical that the thermal penetration depth, Δp , does not exceed the distance from the sensor edge to any one of the material's boundaries in order to maintain a semi-infinite boundary condition. The thermal penetration depth can be calculated using Eqn. 4.

$$\Delta p = 2(\alpha t)^{1/2} \quad (4)$$

In Eqn. 4, α represents the thermal diffusivity of the paraffin and t represents the time that the test is run for. In this work, the samples are cylindrical with diameters and heights of 2.8 cm and 1.4 cm, respectively. The maximum thermal penetration depth calculated for any test in this study is 0.8 cm. Given that the radius of the sensor is 3.189 mm, the maximum allowable thermal penetration depth is ~1.08 cm. Thus, all of the samples in this study can be considered semi-infinite and therefore abide by the geometric constraints of the technique.

The accuracy of the TPS method also depends on the length of time that the test is run for. This time is referred to as a characteristic time and can be calculated based on the TPS sensor geometry and the surrounding material's thermal properties ($t_c = r^2/\alpha$, where r is the radius of the

sensor). When the characteristic time is between $0.33 \leq t_c \leq 1.0$, the solution to the differential equation describing heat flow from the sensor to the surrounding material is insensitive to the curve fitting procedures that are used to relate the data to the solution for the non-linear differential equation [26]. However, significant error results when calculating a solution for the thermal conductivity of the surrounding material if the characteristic time does not fall between these values. Consequently, the characteristic time for all of the samples tested in this work is kept within the range of 0.33 to 1.0 in order to ensure that the solution is accurate.

Calculation of Interfacial Thermal Resistance

The primary objective of this study is to manipulate the bulk thermal conductivity of paraffin PCMs by adjusting the contact area between adjacent, percolating CNTs in order to augment the PCM's melt front progression and solidification rates. To determine the physical mechanisms that are responsible for any enhancement or degradation in the thermal conductivity of the bulk PCM, the microscale physics that govern heat flow at nanoparticle interfaces are analyzed through the calculation of the interfacial thermal resistance at MWCNT-MWCNT junctions. To conduct this analysis, the model developed by Foygel et al. [23] is used to calculate the average contact area between individually touching MWCNTs, the number of MWCNT junctions per unit volume and the effective interfacial thermal resistance at an individual MWCNT-MWCNT interface.

Results and Discussion

For this work, the effective thermal conductivity of the MWCNT/paraffin nanocomposite PCMs is determined as a function of volume fraction when the MWCNTs are fully percolating. The thermal conductivity enhancement of the paraffin (η) is given as a function of volume fraction (ϕ) in Fig. 1.

Fig. 1: Thermal conductivity enhancement (η) of paraffin

As shown in Fig. 1, the bulk thermal conductivity of the MWCNT/paraffin nanocomposites increases with increasing diameter. This result is striking due to the expected nature of thermal transport within the CNTs themselves; as the number of graphene layers surrounding the innermost graphene layer increases (and thus as the diameter of the CNT increases), a greater magnitude of boundary scattering between neighboring graphene layers is expected [12]. Consequently, a reduction in thermal transport within the CNT itself is expected when the number of layers is increased. However, the thermal conductivity enhancement of the MWCNT/paraffin composites is shown to increase with increasing diameter. Thus, simple mixing rules based on the thermal conductivity of the nanoparticles and the surrounding matrix material themselves (represented by Eqn. 5) cannot be used as a basis for the design of MWCNT/paraffin nanocomposites when the nanoparticles are percolating.

$$k_e = k_p \phi_p + k_m \phi_m \quad (5)$$

One possible explanation for this discrepancy is that the flow of heat between nanoparticles is impeded by some interfacial phenomenon. In this case, the only physical parameter that is altered is the contact area between the nanoparticles. Thus, the interfacial thermal resistance between contacting nanoparticles is determined as a function of the average contact area (provided in Table 1) between nanoparticles. For this work, the model developed by Foygel et al. [23] is used to determine the interfacial thermal resistance between nanoparticles as a function of average contact area.

According to Foygel et al. [23], the enhancement in the thermal conductivity of a conventional bulk material is a function of the geometric relationship between the nanoparticle fillers, the morphology of the nanoparticle network(s) and the heat flow rate at contacting nanoparticle junctions when the nanoparticles percolate throughout the material. The effective thermal conductivity (σ) is related to these material properties through Eqn. 6.

$$\sigma(\phi, a) = \sigma_0(\phi - \phi_c)^{t(a)} \quad (6)$$

In Eqn. 6, σ represents the effective thermal conductivity of the paraffin nanocomposite, a is the aspect ratio of the nanoparticles embedded within the host material, σ_0 is a preexponential factor that depends on the thermal conductivity and morphology of the contacting nanoparticle networks, ϕ_c is the volume fraction at which the nanoparticles first begin to form percolating networks and $t(a)$ is a conductivity exponent that depends on the aspect ratio of the nanoparticle. Because there are two unknown parameters in Eqn. 5 (σ_0 and $t(a)$), an iterative scheme is employed in order to produce a best fit trend to the data obtained for effective thermal conductivity using the TPS technique. These parameters can then be used to solve for the effective interfacial thermal resistance between a set of contacting nanoparticles according to Eqn. 7.

$$R_0 = (\sigma_0 \cdot \lambda \cdot \phi_c^{t(a)})^{-1} \quad (7)$$

In Eqn. 7, R_0 is the effective interfacial thermal resistance between two contacting MWCNTs and λ is the average distance between MWCNT junctions. The curve fits for each of the distributions in Fig. 1 are provided in Figs. 2 (a) through (d).

(a) 7 nm MWCNTs

(b) 10 nm MWCNTs

(c) 40 nm MWCNTs

(d) 65 nm MWCNTs

Fig. 2: Curve fits for: (a) MWCNTs with average diameter = 7 nm, (b) MWCNTs with average diameter = 10 nm, (c) MWCNTs with average diameter = 40 nm and (d) MWCNTs with average diameter = 65 nm using the model developed by Foygel et al. [23]

According to the curve fits in Figs. 2 (a) – (d), the conductivity exponent ($t(a)$) is determined to be ~ 1.3 for each of the distributions. While this value was previously calculated to be valid for spherical nanoparticles [23], [27], it is expected that the nanoparticle networks first begin to cluster into larger microspheres prior to percolation [28]–[31].

Using the curve fits that are calculated in Figs. 2 (a) – (d), the interfacial thermal resistance can be calculated using Eqn. 5. The calculated values for interfacial thermal resistance between individual MWCNTs within paraffin is given as a function of contact area in Fig. 3.

Fig. 3: Effective interfacial thermal resistance at MWCNT-MWCNT junctions as a function of overlap area

As shown in Fig. 3, the interfacial thermal resistance between contacting nanoparticles decreases as a function of increasing contact area. Note that the dashed line in Fig. 3 does not constitute a quantitative analysis of a trend between data points, but instead represents a qualitative illustration of the data. In this figure, the interfacial thermal resistance is shown for calculations made by both the Foygel et al. [23] and Wemhoff [32] models. Here, both models are in good agreement with each other, which increases our confidence in the quantitative assessment of interfacial thermal resistance given the different physics with which each model is constructed. Interestingly, the effective interfacial thermal resistance decreases by a factor of ~ 13 as the overlap area increases from 270 nm² to 16,500 nm². One possible explanation for this reduction is the decrease in the ballistic contribution to interfacial thermal resistance at larger interfaces that are formed between contacting CNTs. The relative contributions from ballistic and diffusive transport across the interface can be determined using the analyses provided by Prasher [33]. Both the diffusive and ballistic components of heat flow at the MWCNT/MWCNT interface can be described by Eqns. 6 and 7.

$$R_d = \frac{1}{4 \cdot k_p \cdot b} \quad (6)$$

$$R_b = \frac{4l}{3k_p A_c} \quad (7)$$

In Eqn. 6, b represents the effective diameter of the contact area between individual nanoparticles (nm), A_c represents the contact area at the junction and l represents the mean free path of phonons (nm) within each CNT. In the analysis provided by Wemhoff [24], the contact geometry is assumed to be rectangular. In this work, the contact geometry is assumed to be rectangular with equal dimensions (i.e. a square) for simplicity. Based on these assumptions, a nanoparticle-nanoparticle contact width can be extracted based on the analyses of Prasher [32] and Bahadur et al. [34] modified to fit the constraints of the contacting geometry encountered in this work. The calculated contact widths and areas are provided in Table 3. Additionally, the mean free path of phonons within each MWCNT as well as their effective, intrinsic thermal conductivities are calculated using the Wemhoff model [24] and also listed in Table 3.

Diameter (nm)	Length (μm)	Contact Width, b (nm)	Contact Area, A_c (pm^2)	k_p (W/mK)	λ_c (nm)
7	20	0.016	81	32.8	4.4
10	50	0.022	169	44.2	8.2
25	15	0.038	225	69.1	13.0
65	15	0.098	1681	89.1	16.7

Table 3: Line contact widths and areas at MWCNT/MWCNT junctions

At first glance, the intrinsic thermal conductivity of each MWCNT appears to be low relative to the majority of results presented in the literature [12]. However, the thermal conductivity of an sp^2 hybridized carbon nanoparticle is known to scale as $k \sim \ln(n)$, where n is the number of graphene layers that surround the inner/bottom-most graphene layer, when the nanoparticle rests on (or is embedded within) a surrounding material [35]. In this configuration, the nanoparticle's intrinsic thermal conductivity is also known to be lower than the value for bulk graphite until a critical number of channels for thermal transport are available such that the value for the thermal conductivity of bulk graphite is reached. Consequently, the values for thermal conductivity in Table 3 are not entirely unexpected. The line contact widths in Table 3 are calculated using the diameter-dependent bending moduli supplied by Poncharal et al [36]. Additionally, the interaction energy between the two cylindrical nanoparticles is assumed to take the following form:

$$U(l) = -\frac{3}{8}\pi \cdot A_h \cdot \frac{R^4}{(2R+l)^5} \cdot \left[1 + \frac{25R^2}{(2R+l)^2}\right] \quad (8)$$

329

330 In Eqn. 8, A_h is the Hamaker Constant, l is the separation distance between the nanotubes (0.6
 331 nm [22]) and R is the radius of the nanotube ($D/2$). To find the van der Waals force exerted by
 332 one MWCNT on the other, Eqn. 8 is differentiated with respect to the separation distance, l . The
 333 line contact width is subsequently calculated using Eqn. 9.

334

$$335 \quad b = \frac{1}{2} \cdot \left(\frac{16 \cdot F_{vdw} \cdot E_m \cdot D}{\pi} \right)^{1/2} \quad (9)$$

336

337 Given that the mean free path of phonons (λ) in sp^2 hybridized carbon is on the order of microns
 338 [35] (and that the lowest mean free path in MWCNTs found experimentally to date is 20 nm),
 339 energy carriers are expected to traverse across MWCNT contacts ballistically (i.e. $\lambda \gg b$). Thus,
 340 the primary constriction resistance ($R_{constriction}$) and thermal conductance ($G=1/R_{constriction}$) can be
 341 calculated using Eqn. 7. The thermal conductance at the contacting region (G) is shown as a
 342 function of contact area (A_c) in Fig. 4.

343

344

345 **Fig. 4:** Thermal conductance at MWCNT/MWCNT contacts as a function of contact area

346

347 Figure 4 reveals that the thermal conductance (that is, the amount of heat that can traverse
 348 through the nanoparticle contact) increases by a factor of 27 as the contact area between
 349 MWCNTs increases from 81 pm² to 1681 pm².

350

351 As a consequence of these physical phenomena, fundamental alterations to the adhesion energy
 352 (i.e. the strength of the bond between nano materials) must be improved in the future if thermal
 353 engineers are to further increase the thermal conductance across CNT interfaces.

Recommendations for future research in this area include the application of wrapped polymers [37] and atomic layer deposition (ALD) treatments [38] at the nanoparticle interfaces in order to strengthen the chemical bonding between individual, contacting nanoparticles. This is expected to allow engineers to move toward the full utilization of the unique physics of nanoparticles in macroscopic applications. Additionally, it will also allow scientists and engineers to determine the relative contributions of the adhesion energy and contact area between touching nanostructures on the heat flow between them when used in conjunction with the work done in this study.

Conclusions

In this study, MWCNTs with different diameters are used to produce percolating nanocomposite phase change materials (PCMs). It was found that nanoparticles with smaller diameters produce PCMs with lower thermal conductivities than nanoparticles with larger diameters. This is in contrast to predictions that can be made with effective medium approximations when it is assumed that nanoparticles with smaller diameters have higher thermal conductivities. Using microscale analytical techniques, it is determined that the magnitude of impeded heat flow at the junction increases as a function of decreasing contact area. This is found to be due to the increase in ballistic phonon scattering at the interface as the contact area between nanoparticles decreases. Consequently, the contact area between nanoparticles is found to play a significant role in heat flow at the microscale, resulting in a significant augmentation in the bulk thermal conductivity of percolating nanocomposite PCMs.

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