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Processing of Single-Walled Carbon-Nanotube Metal Matrix Composites and a Finite Element Model for the Process

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In the present investigation, single-walled carbon nanotube (SWCNT or SWNT) reinforced titanium (Ti) matrix composites have been produced by powder metallurgy (PM) and induction heating methods. It has been found that a nickel coating and a fast processing time associated with the induction heating method enables carbon nanotubes to survive the high-temperature (above 1950 K) processing conditions. The result has been a Ti-SWCNT metal-matrix composite (MMC) which is three times stronger and harder than Ti alone, a consequence that has never been accomplished before. This is a promising new development in the application of SWCNT technology to materials science. A mathematical model is given to support the experimental findings.
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Table of Contents

1. Experimental Results .................................................. 1-26
   Introduction ...................................................................... 1
   Procedure ....................................................................... 4
   Results .......................................................................... 21
   References .................................................................... 22-27

2. Computational results ..................................................... 28-58
   Analysis .......................................................................... 28
   Steady-State FEM Analysis .............................................. 33
   Newton-Raphson Method for the Nonlinear Problem .......... 36
   Time Dependence – Newmark’s Method ......................... 42
   Radiation ........................................................................ 44
   Results and Calculations ............................................... 46
   Conclusions .................................................................... 54
   References .................................................................... 55-59

3. Conclusion ........................................................................ 60

4. Appendix A – Wiedemann-Franz Law from the Boltzmann Equation ... 62-66
   References .................................................................... 66

5. Appendix B – Velocity of Propagation: Parabolic versus Hyperbolic
   Differential Equations ..................................................... 67-71
   References .................................................................... 71
1. Experimental Results

Introduction

In the present investigation, single-walled carbon nanotube (SWCNT or SWNT) reinforced titanium (Ti) matrix composites have been produced by powder metallurgy (PM) and induction heating methods. It has been found that a nickel coating and a fast processing time associated with the induction heating method enables carbon nanotubes to survive the high-temperature (above 1950 K) processing conditions. The result has been a Ti-SWCNT metal-matrix composite (MMC) which is three times stronger and harder than Ti alone, a consequence that has never been accomplished before. This is a promising new development in the application of SWCNT technology to materials science.

The discovery of carbon nanotubes [1] has made these structures with nanometer dimensions promising and exciting areas of research. It has been demonstrated by both theoretical calculations and experimental measurements that due to their unique structure individual SWNTs and SWNT ropes display remarkable electrical, thermal, and mechanical properties [2]. Accordingly, these properties make SWNTs excellent additives for composites [3-6].

The addition of single-walled carbon nanotubes (SWCNTs or SWNTs) as fiber reinforcements to make MMCs has been of considerable interest in recent years. Although the addition of SWCNTs to polymers has been more extensively covered, the addition of SWCNTs to metals to form MMCs is a relatively new topic in comparison to polymers [5-6]. A number of reasons can be attributed to this and the main reason is due
to temperature. Polymers can be processed at much lower temperatures than metals using traditional ovens. Therefore, the carbon nanotubes are less likely to react chemically with the matrix. Also, the manufacturing at lower temperatures makes the nanotube much less likely to bond with atmospheric components like oxygen to form molecules such as carbon dioxide or carbon monoxide. The addition of SWCNTs to form MMCs, on the other hand, requires a higher temperature and is plagued with the fact that the resulting composite is usually a metal carbide because the SWCNTs are destroyed in the process.

The principal goal of the experimental portion of this research was to determine a process that would not destroy the SWCNTs in a fully melted carbide forming metal-matrix and to evaluate the resulting composite. Electromagnetic heating was found to accomplish this because of its ability to melt metals rapidly. Rapid heat transfer enables the possibility for the metal to be heated very quickly without reacting with the Carbon composing the nanotube. For metals that do not form carbides, this may not make any difference. However, for carbide forming metals such as Iron, Titanium, and Tungsten, the effect of time is significant. Time, in turn, is related to relaxation time which will be introduced and addressed in the mathematical analysis that follows in Chapter 2 of this thesis. If a conventional oven is used to heat the composite by convection, this could take up to a few hours and the metal would most certainly react with the Carbon content of the SWCNTs. Therefore, electromagnetic heating was used in this work as the means to manufacture the newly-formed MMCs. In order to maximize the potential for a SWCNT to survive in a high-temperature carbide-forming atmosphere, a thin metal coating was used. This metal coating provided a boundary between the carbide-forming metal and the carbon nanotubes.
It is the focus of this research to concentrate on the manufacturing of SWCNTs in a Titanium environment using a metal coating around the nanotube in conjunction with a fast processing time associated with the induction heating method. The resulting metal-matrix composite is new in its composition and manufacturing method. In the second part of this work, a mathematical formulation will be given to model the temperature response in the metal coating and to relate the result to relaxation time. The manner in which the governing equations are presented according to the given boundary conditions is a new contribution to the heat transfer field.
Procedure

The SWCNTs were purchased from Carbon Nanotechnology, Inc. This commercial material contains a 4wt% Fe catalyst as stated by the manufacturer. It should be noted that the manufactured nanotubes were actually a combination of SWCNTs (~33%), double-walled nanotubes (~33%) and multi-walled nanotubes (~33%). They will be referred to as SWCNTs for the remainder of this study. These SWCNTs were nickel (Ni) coated via the electroless plating method [7-12]. A preliminary step in the electroless plating process consists of functionalizing the tubes with Fluorine (creating F-SWCNTs). Then a mixture of Ti powder (~144 μm) along with 0-4.5%wt of these Ni-coated nanotubes was mixed by 15 hours of ball milling [13-16] in isopropanol alcohol. When using copper, the powder size was ~2 μm and 0-1%wt Ni-coated SWCNTs was used.

The purpose of ball milling was to create a mixture where the SWCNTs had been better dispersed in the metal powder as observed by Scanning Electron Microscopy imaging (SEM). These well-mixed final samples were slowly cold-pressed under a pressure of 100 MPa for 10 minutes [17-19]. The resulting sample size was a cylinder 0.635 cm in diameter and 1.9 cm in height weighing about 1.5 grams. The mixed final product can be seen in Figure 1.1 [20].

The SEM picture in Fig. 1.1 illustrates the microstructure of a premixed Cu/SWCNTs sample, showing that the SWCNTs were successfully pre-dispersed among the Cu particles and some SWCNTs were already untangled from bundles and attached onto the particles surface after 10 hrs ball milling without any surface modification or damage. However, some SWCNTs were still entangled to each other forming a thin sheet covering the Cu particles surface.
Figure 1.1. Scanning electron microscopy images (SEM) of SWCNTs/Cu particles after ball milling and before pressing [20].

Originally, only about 20 MPa was used to press the copper powder. Unfortunately, when the electromagnetic heating was used to melt the sample, poor heating was seen. Sintering at 1073 K in Argon was used to improve the electrical conductivity of the sample, and this greatly improved the ability to heat the sample.

Figure 1.2 shows the microstructure of the composites sample after Argon treatment and high temperature sintering but before electromagnetic heating. It is observed that the necks between particles grow, therefore the distance between copper particle centers decreases. The principal driving force for the shrinkage is surface tension which causes transport of material from surfaces with a small radius of curvature to those with a larger radius of curvature. These forces also cause a decrease in the total surface of the pores and thereby shrinkage of the compact. The SWCNTs in the SEM image of the composite samples sintered at 800 °C are similar to those of the premixed material as
shown in Fig. 1.1. No significant change either in morphology or in microtexture is observed.

![SEM image of SWCNTs](image)

**Figure 1.2.** SEM images of SWCNTs after sintering [20]. The arrows point to nanotubes.

Other methods, such as conventional ovens, were used to heat the samples while still following the same mixing and pressing powder metallurgy procedure. Attempts were also made to use pristine uncoated SWCNTs. From experimental observations, it was noticed that in conventional convection ovens, which take hours to heat to the melting temperature of titanium, the SWCNTs would react chemically with the titanium and destroy the structural integrity of the nanotubes. It was also observed that no uncoated nanotubes survive in a titanium environment as temperatures approach the melting point of Ti. The thin metal coating around the nanotube was essential and acts as a stabilizing mechanism in the form of a sacrificial layer.

Since the heating time was a concern, the samples were then melted by a Radyne EI-40 model radio frequency generator. This generator produces 400-600 A of current at
a single frequency of 400 kHz. The large current and frequency creates an electromagnetic field strong enough to induce a heating eddy current sufficient to melt metals [21-25]. The samples were melted (above 1950 K) in an argon atmosphere up to 30 seconds. Because the strength of the field was insufficient for levitation in the case of titanium, a tungsten (W) wire (shown later not to interact with the matrix) was used to hold the sample. The samples were then broken to reveal fractured surfaces and SEM was used to view the sample microstructure. Some samples were cut with a diamond tip blade and polished to make samples for Vickers hardness testing and to reveal grain structure.

The SWCNTs were then removed from the matrix by dissolving the Ti [26-27] using Hydrofluoric (HF) acid to separate the SWCNTs from the Ti matrix. In the case of the copper matrix sulfuric acid was used. The SWCNTs were next filtered from the matrix using sub-micron filter paper under vacuum, and were analyzed by a number of methods following filtering. It should be noted that the matrix was completely dissolved. Spectroscopic techniques were not used in detail for copper because the formation of copper carbide was not considered. Only spectroscopy for titanium will be discussed in detail.

**Imaging Analysis**

SEM images taken from the fractured surface can be seen in Figure 1.3. The structures which are seen in these images that appear curved are nanotubes. In Figure 1.3 (a) a SWCNT can be observed overlapping 3 other nanotubes. In Figure 1.3 (b) a SWCNT is seen that has made a circular or cylindrical loop. It should be noted that the samples were fractured with a hammer and for some samples liquid nitrogen was used to make the fracture appear more brittle. After viewing the SWCNTs in the matrix (Figure
1.3 a and b), the Ti matrix and the Ni [10] coating surrounding the nanotubes were then dissolved in HF acid leaving only the nanotubes to be recovered (c and d).

![Images of electron microscopy results](image)

**Figure 1.3.** Electron microscopy results for nickel-coated SWCNTs in a SWCNT-Ti MMC. (a) and (b) SEM images of the nanotubes after being collected from the processed Ti matrix. Samples observed were seen following specimen fracture. Thin lines that are curved and coiled on the micrographs are the nanotubes. Thicker lines are multiple CNT fibers also called SWCNT strands, bundles, or ropes. (c) and (d) TEM images at higher resolution depicting CNT morphology.
of the nanotube residue dissolved from the MMC. Reference bars (a) 200 nm, (b) 100 nm, (c) 20 nm and (d) 20 nm are shown respectively [28].

TEM images were also obtained in this study using a JEOL 2010 model transmission electron microscope. Only after collecting the nanotubes from the dissolved Ti, were they imaged. As can be seen in Figure 1.3 (c) and (d) the cylindrical geometry of the nanotubes is still present after processing.

Spectroscopic Analysis

X-ray Photoelectron Spectroscopy (XPS) was used to confirm the composition of the final material unmodified after being dissolved. From Figure 1.4, it can be said that only carbon (C), Ti, fluorine (F) and oxygen (O) are present. More importantly, the inset of Figure 1.4 shows the existence of graphitic carbon with a C peak at 284 eV which agrees with XPS handbook standards [29].

![Graph showing binding energy and intensity](image)

**Figure 1.4.** Full range XPS scan (0-1200 eV) of the collected CNT material after processing dissolved Ti from the MMC [28]. The inset is a scan in the region of
the primary carbon peak (282-286 eV) with a peak value at 284 eV. Intensity is normalized to the highest peak. If TiC were present the C peak would be 281-282 eV according to the same standards. No treatment or preparation was made to the sample before XPS measurements were made. Tungsten is not present, so the interaction of the sample with the tungsten wire used to hold the sample is considered negligible. Since the entire sample was dissolved, the measurements could be from any location from the original sample.

Raman Spectroscopy was also used as a means of confirmation that a Ti-SWCNT MMC was produced and the carbon nanotubes were not compromised in this study. Characterization and comparison of the nanotubes before and after each stage of the production of the MMC and its post-processing to dissolve away the Ti were carried out. This was to establish that the MMC’s nanotube components still survived. All data were taken with a Renishaw Raman RM1000 Spectrometer (780 nm wavelength).

The results can be seen in Figure 1.5 and Figure 1.6. The data comparison consisted of three stages illustrated in Figure 1.5(a) and 1.6(a): pure SWCNTs, Ni coated F-SWCNTs before processing in melted Ti, and the recovered SWCNTs including nanotube ropes after dissolution of the Ti from the MMC as seen in Figure 1.3(c) and 1.3(d). It is important to remember that the latter stage included nanotube material that once existed in a melted Ti environment and was not destroyed.
Figure 1.5. (a) The Raman spectroscopy results for Titanium processed Ni-coated SWCNTs. (b) The amount of Fluorine bonding with the nanotube can vary the Raman result similar to Figure 3 of [10].
Comparison of Raman Results for SWNTs before and after processing in Ti

(a)

Comparison of SWCNTs after processing in Ti vs. TiC and Rutile

(b)

Figure 1.6. (a) Raman Spectra of the SWCNTs before and after processing the SWCNTs in melted Titanium. (b) Raman comparison of TiC, TiO$_2$ and SWCNTs.
No distinct change is evident in Figure 1.5(a) and 1.6(a) between the three stages of comparison – that is, the spectra of the Ni-coated SWCNTs before processing in melted Ti and that of the collected SWCNTs after dissolution from the Ti composite matrix. The existence of a peak below 500 cm$^{-1}$ (labelled by 206.07, 207.16, and 208.275 cm$^{-1}$) in the Raman spectra is indicative of radial breathing modes (RBMs) [30] that characterize resonance excitations and vibrational modes of the cylindrical structure of SWCNTs. This in itself demonstrates the existence and presence of SWCNTs. After melting in the titanium, the character of the cylindrical carbon-carbon bond is still in the radial structure which distinguishes it from graphite [31,32].

Figure 1.5(b) depicts the effects of different levels of the intermediate Nickel coating and flourination. Figure 1.6(b) is a detailed view of the Pure SWCNTS curve in Figure 1.6(a) in the region 100-900 cm$^{-1}$. The SWCNT peak is the same as that in Figure 1.6(a) although the relative intensity has been changed in order to make comparisons with other molecules. Raman spectra were determined for TiC and TiO$_2$ using commercially available samples and the results compared with the Pure SWCNTs in Figure 1.6(b). Both TiC and TiO$_2$ are not present in the three-stage study shown in Figure 1.6(a).

It can therefore be said that the nanotube geometry is not altered during the processing of SWCNTs in the Ti matrix reported here. When SWCNTs are placed in the Ti powder without a coating or without fast induction heating, and the same procedure is followed, the Raman spectroscopy results reveal only TiC as shown in Figure 1.6(b). This demonstrates that the nanotube structure is destroyed in the heating process without a coating, and in the slow oven heating process as was seen by experimental observation.
In summary, a specific comparison of the radial breathing mode given in Figure 1.6 (b) shows the direct comparison between Titanium Oxide, Titanium Carbide, and the SWCNTs. The fact that they are dramatically different confirms the existence of SWCNTs after manufacturing in the melted Titanium and verifies that TiO and TiC did not form.

*Grain structure*

The primary motivation of this study was to create a Ti-SWCNT composite and to explore its implications as a new MMC with increased hardness and strength. With that in mind, evaluation of grain structure was necessary. Grain structure properties have been studied in powder metallurgy using Titanium as the matrix [33] but not for the new composite material presented here. Hence grain measurements were performed to explore the promise of the composite manufactured in this work.

Average grain size measurements were made using the mean lineal intercept method according to the American Society for Testing and Materials (ASTM) standard E 112-88. SEM images are required for this method, and accordingly were taken. Figure 1.7 shows this information. Figures 1.7(a)-(d) indicate that the addition of SWCNTs causes grain growth refinement, which results in a smaller average grain size in the SEM images. This is visible progressively from (a) to (d).
Figure 1.7. Grain structure of the composite material with increasing wt% nanotubes: (a) 0, (b) 0.5, (c) 1.5 and (d) 2.5% SWCNTs respectively. The scale bar is 200 μm and is the same for all four figures. Grain refinement can be seen progressively from (a) to (d).

The change in average grain size as a function of concentration of SWCNTs seen in Figure 1.7 is quantified in Figure 1.8 which was determined using the previously mentioned ASTM standard. As can be seen, the grain size is decreased by the addition of nanotubes [34-36] for the cases examined here. The line of best fit is shown with the experimental measurements given as a polynomial spline-function interpolation only and does not
represent actual data. The error bars in Figure 1.8 indicate the variation in the measurements taken to one standard deviation above and below the average value.

![Grain Size](image.png)

(b)

**Figure 1.8.** Titanium grain size vs. weight-percent addition of Ni-coated SWCNTs with a spline-function fit.

**Vickers hardness analysis**

It is well known that hardness is not an intrinsic property of a material, but is an empirical parameter determined by a certain experimental procedure and method whose value is directly related to strength through a scaling transformation. Hence hardness data is often seen used interchangeably with stress and strength data as a function of grain size in the Hall-Petch relationship [37-44].
Hardness data for the MMC examined here were obtained as follows. The starting powder size in this analysis was ~140 microns as can be seen using Figure 1.8. After cutting samples of the Ti composite with a diamond-tip saw blade and polishing the resultant surfaces, measurements using a 10 g weight were made on those surfaces. In most microhardness tests 10 g might be considered small, but it was used here because it made an indentation of approximately 5-12 microns. As seen in Figure 1.8, the smallest grain size obtained was 39.7 microns. Similar results to those in Figure 1.8 were obtained with a 25 g weight.

The addition of SWCNTs beyond 1 %wt. for Copper and 4.5% wt. for Titanium was not considered because of difficulty found with preform expansion during heating. As grain size is reduced through the nanometer regime (< 100 nm), hardness typically increases with decreasing grain size and can be factors of two to seven times harder for pure nanocrystalline metals (10 nm grain size) than for large-grained (> 1 μm) metals [39]. A 2.88 times increase in hardness (188% increase) was found here in the conventional Hall-Petch regime.

The Vickers measurements are summarized in Figure 1.9. The data values as a function of weight-percent are shown, and it can be seen that Vickers hardness value (HV or HV) improved with increasing addition of SWCNTs. The spline-function fit and error bars are similar to Figure 1.8.
Figure 1.9. Vickers hardness vs. weight-percent addition of Ni-coated SWCNTs with a spline-function data fit: in (a) Copper and (b) Titanium [28].
Figure 1.10 depicts the HV hardness data as a Hall-Petch plot in units of kilogram-force per square millimeter plotted against inverse square-root of grain size $d$ (actually $d^{-0.5}$) rather than against weight-percent as in Figure 1.9.

![Vicker's Hardness vs Grain Size diameter parameter](image)

**Figure 1.10.** Hall-Petch plot of Vickers hardness vs. inverse square-root grain size ($d^{0.5}$). The data fall in the conventional Hall-Petch regime (diamonds ⭐). Hall-Petch breakdown in the nanocrystal regime (triangles ▲) depends upon slope and is of three types: (i) positive; (ii) zero; and (iii) negative slope. Only (iii) negative slope is depicted. In the single crystals regime (squares □), positive curvature is evident and the power of $d$ changes to $d^{0.8}$ (e.g., Shulson [40] and Farhat [44]).
3. Discussion

In order to put the hardness results from this study into better perspective with respect to current ideas and understanding of hardness and strength, the experimental results in Figure 1.10 need further discussion. Hardness and strength are a function of grain size for conventional crystalline materials ($d > 1 \, \mu m$). The Hall-Petch law [37] expresses the grain-size dependence of flow stress for plastic strain out to ductile failure. That is, it states that grain-size dependence of macroscopic plastic yield stress $\sigma_y$ of a polycrystal is given by $\sigma_y = \sigma_0 + kd^{1/2}$ where $d$ is the grain size, while $k$ and $\sigma_0$ are constants. Sometimes $\sigma_0$ is called friction stress. In the literature $\sigma_y$ is often referred to as yield strength rather than yield stress. Similar empirical results have been found for hardness$^{37,42}$ with $H_V = H_O + kd^{1/2}$ where $H_O$ is the functional hardness equivalent of friction stress when scaled to hardness units. Experimental results from hardness measurements have found different behavior for dependence on grain size at the smallest nanocrystalline grains ($< 20 \, \text{nm}$). These include (i) a positive slope or “normal” Hall-Petch behavior), (ii) essentially no dependence or zero slope, and (iii) a negative slope. Under such circumstances, the Hall-Petch law has broken down [39]. This information is included here because of its relation to nanocrystals of Ni around the SWCNTs. From Figure 1.10 it is clear that the data obtained is related to the Hall-Petch equation and that Hall-Petch breakdown did not occur. Future research can be performed by other groups starting with commercially available nanocrystalline Ti powder to study the effects in the nanoscale area ($d^{-0.5} < 0.09$).

The Louchet et al. [37] examination of the breakdown of Hall-Petch has given new insight into the effect of grain size on plastic yield stress. In Figure 2 of their paper,
the schematic regime for Hall-Petch breakdown is identified. The expected behaviors in Figure 1.10 are identical to Figure 2 of Louchet and the obtained data coincide with the Hall-Petch regime. Yield stress and hardness behavior for nanocrystals \( d^{0.5} > 0.16 \) deviate from the Hall-Petch equation. Only the expected case for negative Hall-Petch behavior (negative slope) is depicted. For larger grain size (single crystals, \( d^{0.5} < 0.09 \)), the figure has been extended as shown in Shulson [40], Farhat [44], and Louchet [37]. In this region the power of grain-size dependence \( n \) has been shown by Shulson, using a regression analysis, to change to \( kd^n \) with \( n \neq 0.5 \) as the yield stress \( \sigma \), approaches the friction stress \( \sigma_\infty \) and the hardness approaches \( H_0 \). Although the Shulson result may only be a special case, the method of regression analysis remains relevant.

**Results**

SWCNTs were incorporated into Copper and Titanium matrices using a rapid heat transfer technique made available by electromagnetic heating technology. The addition of SWCNTs was verified through imaging (SEM and TEM) and spectroscopic (XPS and Raman) techniques. Composite property evaluations such as gain size and Vickers Hardness were made and shown to be indicators of strength increase as a function of nanotube addition. Currently sample sizes are limited to roughly 25-50 grams. A scale-up of this manufacturing process could lead to industrial sized production samples.
References:


Chapter 2. Computational Results

Analysis

After imaging and spectroscopic evidence in Chapter 1 confirmed the existence of the SWCNTs which were removed from the Titanium matrix, a number of questions arose. It was known that the addition of SWCNTs to the Titanium matrix without a Nickel coating would produce Titanium Carbide, and that no SWCNTs would be present after processing. It was also shown that slow heating times in a conventional oven resulted in the same production, Titanium Carbide. It was then realized that the rapid heat transfer technique available with the electromagnetic heating method produced the desired Ti-SWCNT MMC result using Nickel-coated SWCNTs.

When the coating was added to the outside of the SWCNT and then placed in the matrix, the spectroscopic results confirmed that the nanotubes were still present in their cylindrical structure. The addition of the Nickel coating was clearly the reason the SWCNTs survived inside the matrix during rapid heat transfer at the high-temperature conditions. Two logical explanations for the survival of nanotubes arose. The first idea was that the coating acted as a chemical barrier. If the Nickel separated the Titanium from the Carbon, then there were no Carbon atoms which could form with the Titanium and Titanium Carbide could not be present. Another possible explanation was that the Nickel coating served as a thermal barrier impeding heat transfer and limiting the temperature rise of the nanotubes.

The idea that the coating acts as a thermal barrier relies on the powder being the carrier of heat. From a microscopic stand point, if one looks at the nanotubes in the powder before processing, it would be observed that the nanotubes are basically
suspended between powder particles (Figures 1.1-1.3). Since they are so small compared to the powder size (the SWCNTs, with the coating, are 10-200 nm in diameter, and 100 nm -3 microns long while the powder can be thought of as a sphere (Figures 1.1-1.2) of radius ~100 microns), the nanotubes will certainly not be the main carriers of heat in the powder metallurgy process. It is the powder which is responsible for the heat transfer. It became obvious that a detailed analysis would be needed to understand the behavior of rapid heat transfer in a thin film such as the coating around the SWCNTs. Fortunately, a number of studies have been made to understand the physics of thin films [1,2]. In this particular study, a number of known relationships will be used to understand better the temperature response of a thin metal film.

It is known that the electrical resistivity $\rho_r$ of a thin film is a function inversely proportional to grain size. For a metal, the mean free path of a conducting electron is $\sim$1-50 nm at room temperature. According to Fuchs and Sondheimer [1-2], the electrical resistivity of a metal film is a function of the ratio of the mean free path to the grain size diameter and can be expressed as

$$\rho_r(d) = \rho_0 \left[ 1 + \frac{l}{d}(1 - p) \right]$$

(2.1)

where $\rho_0$ is the bulk resistivity of the metal, $l$ is the electron mean free path, $p$ is a scattering parameter with values between $0 \leq p \leq 1$ (here it will be assumed that the scattering parameter is always $p=0$, corresponding to diffuse scattering), and $d$ is the grain size diameter. This result was originally given by Fuchs [1,2], and it was determined both by analytical derivation as well as experimental results. It has since been studied elsewhere [3].
From Equation (2.1), it can be seen that as the grain size diameter goes to zero or the mean free path becomes larger, then the electrical resistivity becomes larger as a direct result of increasing electron mean free path or decreasing grain size. The Nickel coating on the SWCNTs was processed via electroless plating. The diameter of the coating on the nanotubes is no more than 50 nm as can be seen from SEM images [Fig. 1.1]. Since the diameter is ~50 nm, it is assumed that the grain size can be no more than 25 nm by symmetry (this is a largest-case situation; it is known the grain size can be smaller). Recall that the mean free path can be as much as 40 nm. This implies that the electrical resistivity of the thin film must be at least triple that of the bulk resistivity when Equation (2.1) is taken into consideration. It can be observed that in many applications of nanotechnology the grain size might be on the order of 1 nm and in some cases, slightly below a nanometer [4-21]. For a material with an electron mean free path of 40 nm, the electrical resistivity of the material then becomes over 40 times greater than that of the bulk measurement due to grain size variation alone.

The Wiedemann-Franz law is another empirical equation that relates the ratio of the thermal and electrical conductivities to the temperature (as from the Boltzmann equation, Appendix A). It is given by

\[
\frac{k}{\sigma} = L_n T
\]

where \( k \) is the thermal conductivity, \( \sigma \) is the electrical conductivity (which is equal to the inverse of the resistivity, \( \sigma = 1/\rho \)), and \( L_n \) is a constant (2.44x10^-8 WΩK^-2) known as the Lorenz number. It holds true in a variety of cases for solid metals, semiconductors, and liquid metals [17]. The thermal conductivity then becomes:
\[ k = \alpha L_n T \quad \text{or} \quad k = \frac{1}{\rho_r} L_n T. \quad (2.3) \]

Recall that the resistivity of the metal in Equation (2.1) is actually a function of electron mean free path and grain size diameter. The thermal conductivity can now be written as:

\[ k = \frac{L_n T}{\rho_{r_0} \left[ 1 + \frac{l}{d} (1 - p) \right]} . \quad (2.4) \]

From our previous assumptions of 1nm grain size, it can be seen that the thermal conductivity of a thin film can be 40 times higher than that of the bulk material, just by varying the grain size. When considering this in heat transfer analysis, it is apparent that for small grain size, the inclusion of grain size can be very important and would cause significant errors during analysis if it is neglected. For this study, with a given grain size and zero scattering, we will adopt the constant:

\[ L_0 = \frac{L_n}{\rho_{r_0} \left[ 1 + \frac{l}{d} (1 + p) \right]} . \quad (2.5) \]

When considering the heat transfer in a thin film, another aspect that must be included is the velocity of propagation or propagation speed. Heat actually propagates as a wave. However, in Fourier heat conduction the speed of that wave is assumed to be infinity, a circumstance that has to be rectified (Appendix B). The most general governing equation for time-dependent heat transfer according to Fourier conduction can be seen in Equation (2.6) which includes a source or generation term \( g \).

\[ \frac{\partial}{\partial x} \left( k \frac{\partial T}{\partial x} \right) + g = \rho c_p \frac{\partial T}{\partial t} . \quad (2.6) \]
Here, $T$ is the temperature, $k$ is the thermal conductivity, $\rho$ is the density, $c_p$ is the specific heat, $x$ is the space variable, and $t$ represents time.

A more accurate description of the propagation of heat in a medium would be to include information about the rate at which heat propagates. The problem of heat transfer by electrical currents in conducting media having a relaxation time $\tau$ was addressed some time ago and appears in electrical engineering textbooks as the telegraph equation or the “equation of telegraphy” [22], [Appendix B, Equation (B1b)]. In fluid mechanics, this equation was first considered by Cattaneo [23] although it is actually a simplification of the Jeffrey’s equation [24]. Cattaneo investigated non-Fourier conduction by including the second-order time derivative in the conduction equation:

$$\frac{\partial}{\partial x} \left( k \frac{\partial T}{\partial x} \right) + g = \rho c_p \left( \frac{\partial T}{\partial t} + \tau \frac{\partial^2 T}{\partial t^2} \right).$$

(2.7)

All the variables are the same in Equation (2.7) as they are in (2.6) except that a phenomenological relaxation-time parameter $\tau$ has been introduced. The velocity of thermal propagation $v$ is now finite (Appendix B) and can be written as $v = (\rho c_p / \tau)^{1/2}$. In the diffusion limit, $\tau \to 0$, Fick’s laws are recovered with an infinite $v$.

Equation (2.7) is known as the hyperbolic heat conduction equation, Non-Fourier heat conduction equation, or the Cattaneo equation and has been studied in the literature by a number of different authors [24-34]. This changes the nature of the partial differential equation from parabolic to hyperbolic and eliminates the pathological problem inherent in Fourier’s or Fick’s law. Since the addition of the term is still linear, the analysis of non-Fourier heat transfer is not greatly complicated compared to Fourier analysis. A review of thermal conductivity in thin films and a discussion of their importance to engineering applications can be found in [35].
After substitution of the Wiedemann-Franz (WF) law for thermal conductivity into the governing equation for heat conduction we obtain:

$$\frac{\partial}{\partial x} \left( L_0 T \frac{\partial T}{\partial x} \right) + g = \rho c_p \left( \frac{\partial T}{\partial t} + \tau \frac{\partial^2 T}{\partial t^2} \right).$$  \hspace{1cm} (2.8)

The substitution of the WF law complicates Equation (2.7) giving Equation (2.8). If the thermal conductivity is considered to be a constant as in Equation (2.7), the analysis of the equation depends on solving a linear hyperbolic partial differential equation. However, the substitution of the WF causes the analysis to become a nonlinear hyperbolic differential equation. The general solution to the parabolic case was given in [36] subject to constant heat flux and without consideration of any generation term. Grain size was not considered in that study.

The procedure for solving Equation (2.8) using the Finite Element Method (FEM) will be given here. The FEM is used here only as a tool to study and solve the equations, but this is not a study in finite element methods. More detailed discussions of the FEM can be found elsewhere [37-39].

**Steady-State FEM Analysis**

In order to solve Equation (2.8) using the FEM, we will first analyze the computational material, and then consider time dependency [37]. The 1-dimensional steady-state equation for heat conduction including the substitution into the Wiedemann-Franz law follows from Equation (2.8):

$$\frac{d}{dx} \left( L_0 T \frac{dT}{dx} \right) + g = 0; \quad 0 < x < L, \hspace{1cm} (2.9)$$
noting that relaxation-time effects disappear as expected. This equation (now an ordinary differential equation instead of a partial differential equation), for the present study, is subjected to the following boundary conditions (other boundary conditions will be considered in later sections of this work such as constant temperature):

\[ L_0 T \frac{dT}{dx} \bigg|_{x=0} = -g_0 = P_1 \quad (2.10) \]

\[ L_0 T \frac{dT}{dx} \bigg|_{x=L} = h(T_{\infty} - T(x=L)) = P_2 \quad (2.11) \]

For now, \( P_2 \) will be considered a constant. The fact that it is actually a function of temperature will be included shortly. It should be noted that these boundary conditions must simulate the experimental boundary conditions for the Nickel-coated SWCNTs. In the case of the SWCNTs, the metal coating annulus has an inner surface subjected to a constant heat flux boundary condition \((g_0=\theta \text{ due to symmetry})\), and the outer surface is subject to the convective and radiation boundary condition.

At this point the actual analysis of the FEM can begin by starting with the steady-state equation for nonlinear heat transfer, Equation (2.9). For now, a 2-node element will be considered. It will then be shown how to expand this to \( N \) elements. The governing differential equation is subsequently multiplied by the weighting function, \( w_i \). Writing the integral over the element and then integrating by parts, the weak form of the equation is given by:

\[ \left[ \left( \frac{dT}{dx} \right) w_i \right]_{x=L} - \left[ \left( \frac{dT}{dx} \right) w_i \right]_{x=0} + \int_0^L \left( - \left( \frac{dT}{dx} \right) w_i + \frac{g}{L_0} w \right) dx = 0. \quad (2.12) \]

After applying the given boundary conditions, the following is obtained:

\[ 34 \]
\[ P_1 w_1(x_1) + P_2 w_2(x_2) + \int_{x=0}^{x=L} \left( -\left( T \frac{dT}{dx} \right) \right) w' + \frac{g}{L_0} w \, dx = 0 \]  

(2.13)

The two node element problem assumes the solution is a linear interpolation of the two nodal unknowns:

\[ T(x) = \begin{pmatrix} x-x_2 \\ x_1-x_2 \end{pmatrix} \frac{1}{x_1-x_2} \begin{pmatrix} T_1 \\ T_2 \end{pmatrix} = \begin{pmatrix} N_1 & N_2 \end{pmatrix} \begin{pmatrix} T_1 \\ T_2 \end{pmatrix}, \]

(2.14)

with the functions \( N_1 \) and \( N_2 \) given by:

\[ N_1 = \frac{x-x_2}{L}; \quad N_2 = \frac{x-x_1}{L}. \]

(2.15)

Here, \( L \) is the length of the element.

The derivative of the function used in Equation (2.13) is then:

\[ T'(x) = \frac{dT(x)}{dx} = \begin{pmatrix} 1 \\ x_1-x_2 \end{pmatrix} \frac{1}{x_1-x_2} \begin{pmatrix} T_1 \\ T_2 \end{pmatrix} = \begin{pmatrix} N_1' & N_2' \end{pmatrix} \begin{pmatrix} T_1 \\ T_2 \end{pmatrix}. \]

(2.16)

The derivative depends only on the special derivative of the weighing function:

\[ N_1' = \frac{1}{L}; \quad N_2' = \frac{1}{L}. \]

(2.17)

Now all the necessary information is available to solve Equation (2.9). Here, \( w_i \) is replaced with \( N_i \) and \( P_1, P_2, T, \) and \( T' \) are all known. The result becomes a system of equations for each node in the element (in this case 2):

\[ P_1 N_1(x_1) + P_2 N_1(x_2) + \int_{x=0}^{x=L} \left( -\left( T \frac{dT}{dx} \right) \right) N_1' + \frac{g}{L_0} N_1 \, dx = 0 \]

\[ P_1 N_2(x_1) + P_2 N_2(x_2) + \int_{x=0}^{x=L} \left( -\left( T \frac{dT}{dx} \right) \right) N_2' + \frac{g}{L_0} N_2 \, dx = 0 \]

(2.18)

Using \( N_1(x_1) = N_2(x_2) = 1 \) and \( N_1(x_2) = N_2(x_1) = 0 \) the equation can be simplified to:

\[ \int_{x} \left( \begin{array}{c} g \\ -L_0 \end{array} \right) N_2 - \left( \begin{array}{c} N_1' \\ N_2' \end{array} \right) T'(x) \, dx + \left( \begin{array}{c} P_1 \\ P_2 \end{array} \right) = \left( \begin{array}{c} 0 \\ 0 \end{array} \right). \]

(2.19)
After substitution for $T$ and its derivative, the equation becomes:

$$\int \left( \begin{array}{c} \frac{g}{L_0} \\ N_1 \\ N_2 \end{array} \right) \left( \begin{array}{ccc} N_1' & N_1' & T_1 \\ N_2' & N_2' & N_2' \end{array} \right) dx + \left( \begin{array}{c} P_1 \\ P_2 \end{array} \right) = \left( \begin{array}{c} 0 \\ 0 \end{array} \right). \tag{2.20}$$

The equation will then be written as:

$$k(d) = r_E \tag{2.21}$$

where:

$$k(d) = \int \left( \begin{array}{ccc} N_1' & N_1' & T_1 \\ N_2' & N_2' & N_2' \end{array} \right) dx \tag{2.22}$$

$$r_E = r_q + r_p; \quad r_q = \int \begin{array}{c} N_1 \\ N_2 \end{array} \frac{g}{L_0} dx; \quad r_p = \begin{array}{c} P_1 \\ P_2 \end{array}. \tag{2.23}$$

After integration, the following vectors are obtained:

$$k = \left\{ \begin{array}{l} T_1^2 - T_2^2 \\ T_2^2 - T_1^2 \end{array} \right\} / 2L, \quad r_q = \left\{ \begin{array}{l} \frac{gL}{2L_0}, \\ \frac{gL}{2L_0} \end{array} \right\}. \tag{2.24}$$

**Newton-Raphson Method for the Solution to the Nonlinear Problem**

The Newton-Raphson method for solving nonlinear FEM equations is commonly used. It solves a global set of equations which are nonlinear in terms of the nodal unknowns. Here, we will briefly discuss the Newton-Raphson method, and give an example problem of the global assembly for a 3-element (4-node) case. After assembling all the elements, the system of nonlinear equations for temperature can be written as:

$$K(d) = R_E \tag{2.25}$$

where the following transposes are used:

$$d = \begin{pmatrix} T_1 & T_2 & T_3 & \ldots & T_n \end{pmatrix}^T$$

is the row-vector of unknown temperatures;
\[ K(d) = \begin{pmatrix} K_1(d) & K_2(d) & K_3(d) & \ldots & K_n(d) \end{pmatrix}^T \text{ the nonlinear function vector for } d; \]

\[ R_E = \begin{pmatrix} R_1 & R_2 & R_3 & \ldots & R_n \end{pmatrix}^T \text{ is a row-vector of known quantities,} \]

In Equations (2.25)-(2.50) that follow, note that \( d \) is not to be confused with grain size convention \( d \) or mean-free-path-ratio-to-grain-size \( l/d \) in Equation (2.5). Routine FEM analysis involves the "a-form", "v-form", and "d-form" as a matter of notation in Newmark's method that follows.

The solution for each iteration is approximated using the Taylor series:

\[ K(d^{i+1}) = K(d^i) + K_T \Delta d^i = R_E \Rightarrow K_T \Delta d^i = R_E - K(d^i). \quad (2.26) \]

\( K_T \) is the global tangential matrix and is assembled by:

\[ K_T = \begin{bmatrix}
\frac{\partial K_1(d^i)}{\partial T_1} & \frac{\partial K_1(d^i)}{\partial T_2} & \frac{\partial K_1(d^i)}{\partial T_3} & \ldots & \frac{\partial K_1(d^i)}{\partial T_n} \\
\frac{\partial K_2(d^i)}{\partial T_1} & \frac{\partial K_2(d^i)}{\partial T_2} & \frac{\partial K_2(d^i)}{\partial T_3} & \ldots & \frac{\partial K_2(d^i)}{\partial T_n} \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
\frac{\partial K_n(d^i)}{\partial T_1} & \frac{\partial K_n(d^i)}{\partial T_2} & \frac{\partial K_n(d^i)}{\partial T_3} & \ldots & \frac{\partial K_n(d^i)}{\partial T_n}
\end{bmatrix}, \quad \Delta d = \begin{pmatrix} \Delta T_1 \\ \Delta T_2 \\ \vdots \\ \Delta T_n \end{pmatrix}. \quad (2.27) \]

\( K \) is given from Equation (2.24). The object is to solve Equation (2.26) for the unknown \( \Delta d^i \) and then update the nodal unknowns by:

\[ d^{i+1} = d^i + \Delta d^i. \quad (2.28) \]

The global vector governing the generation term and boundary conditions must be updated also:

\[ R^{i+1} = R_E - K(d^{i+1}). \quad (2.29) \]

As a demonstration, a simple 3-element (4-node) problem will be given. Recall that the form for the general solution can be given by Equation (2.21):


\[ k(d) = r_E. \]

After integration of Equation (2.22), the vector is given by Equation (2.24)

\[
k(d) = \left\{ \frac{T_1^2 - T_2^2}{2L}, \frac{T_2^2 - T_3^2}{2L} \right\}.
\]

For multiple elements, the global vector is assembled by:

\[
K(d) = \left\{ \frac{T_1^2 - T_2^2}{2L}, \frac{T_2^2 - T_1^2}{2L}, \frac{T_2^2 - T_3^2}{2L}, \frac{T_3^2 - T_2^2}{2L}, \frac{T_3^2 - T_4^2}{2L}, \ldots, \frac{T_{n+1}^2 - T_n^2}{2L} \right\}. \tag{2.30}
\]

The external fluxes for each element is given by the integration of Equation (2.24):

\[
r_E = r_q + r_p; \quad r_q = \left( \begin{array}{c} gL \\ \frac{2L_0}{gL} \\ \frac{2L_0}{gL} \end{array} \right); \quad r_p = \left( \begin{array}{c} p_1 \\ p_2 \end{array} \right).
\]

The problem can now be solved. From Equation (2.27), the tangential vector for the first element is given as:

\[
k_T = \left( \begin{array}{cc} \frac{\partial k_1}{\partial T_1} & \frac{\partial k_1}{\partial T_2} \\ \frac{\partial k_2}{\partial T_1} & \frac{\partial k_2}{\partial T_2} \end{array} \right) = \left( \begin{array}{cc} \frac{T_1}{L} & -\frac{T_2}{L} \\ -\frac{T_1}{L} & \frac{T_2}{L} \end{array} \right). \tag{2.31}
\]

The global tangential matrix is assembled as in Equation (2.27). For the 3-element (4-node) problem, the global tangential matrix is given by:

\[
k_T = \frac{1}{L} \left( \begin{array}{cccc} T_1 & -T_2 & 0 & 0 \\ -T_1 & 2T_2 & -T_3 & 0 \\ 0 & -T_2 & 2T_3 & -T_4 \\ 0 & 0 & -T_3 & T_4 \end{array} \right). \tag{2.32}
\]

\( R_E \) is given as:
\[
\begin{align*}
    r_e &= r_q + r_p = \begin{pmatrix}
        \frac{gL}{2L_0} \\
        \frac{gL}{2L_0} \\
        \frac{gL}{2L_0} \\
        \frac{gL}{2L_0} \\
        \frac{gL}{2L_0}
    \end{pmatrix} + \begin{pmatrix}
        P_1 \\
        0 \\
        0 \\
        P_2
    \end{pmatrix}.
\end{align*}
\]

(2.33)

Here the boundary conditions are applied from Equations (2.10) and (2.11).

\[
\begin{align*}
    L_0T \frac{dT}{dx} \bigg|_{x=0} &= -g_0 = P_1 \\
    L_0T \frac{dT}{dx} \bigg|_{x=L} &= h(T_\infty - T(x = L)) = P_2.
\end{align*}
\]

Equation (2.11) is substituted into (2.33), and then (2.21) is solved. It should be noted that for the general case, the correct substitution of (2.11) into (2.21) leads to \(hT_\infty/L_0\) being in \(R_E\) and \(hT(x=L)/L_0\) being in \(K_T\). The second term is moved into the \(K_T\) matrix and only the derivative remains. In this particular equation the term is \(h/L_0\). This can be seen in Equation (2.34) in the \(i\times nth\) entry to the matrix. After applying these conditions to \(K_T\) and \(r_E\) we get:

\[
K_T = \begin{bmatrix}
    \frac{\partial K_1(d^i)}{\partial T_1} & \frac{\partial K_1(d^i)}{\partial T_2} & \frac{\partial K_1(d^i)}{\partial T_3} & \cdots & \frac{\partial K_1(d^i)}{\partial T_n} \\
    \frac{\partial K_2(d^i)}{\partial T_1} & \frac{\partial K_2(d^i)}{\partial T_2} & \frac{\partial K_2(d^i)}{\partial T_3} & \cdots & \frac{\partial K_2(d^i)}{\partial T_n} \\
    \vdots & \vdots & \vdots & \ddots & \vdots \\
    \frac{\partial K_n(d^i)}{\partial T_1} & \frac{\partial K_n(d^i)}{\partial T_2} & \frac{\partial K_n(d^i)}{\partial T_3} & \cdots & \frac{\partial K_n(d^i)}{\partial T_n} + \frac{h}{L_0}
\end{bmatrix}
\]

\[
r_E = \begin{pmatrix}
        \frac{gL}{2L_0} \\
        \frac{gL}{2L_0} \\
        \frac{gL}{2L_0} \\
        \frac{gL}{2L_0} \\
        \frac{gL}{2L_0}
    \end{pmatrix} + \begin{pmatrix}
        \frac{g_0}{L_0} \\
        0 \\
        0 \\
        \frac{h}{L_0} \\
        \frac{T_\infty}{L_0}
    \end{pmatrix}
\]

In the case of Equation (2.32) we finally arrive at:
\[ K_T = \frac{1}{L} \begin{pmatrix} T_1 & -T_2 & 0 & 0 \\ -T_1 & 2T_2 & -T_3 & 0 \\ 0 & -T_2 & 2T_3 & -T_4 \\ 0 & 0 & -T_3 & T_4 + \frac{h}{L_0} \end{pmatrix} \quad \text{and} \quad r_E = r_q + r_p = \begin{pmatrix} \frac{gL}{2L_0} \\ \frac{gL}{L_0} \\ \frac{gL}{2L_0} \\ \frac{gL}{L_0} \end{pmatrix} + \begin{pmatrix} -\frac{g_0}{L_0} \\ 0 \\ 0 \\ \frac{h}{L_0} T_\infty \end{pmatrix}. \]

The initial guess is made for the node values, and they are then updated by solving the following equation:

\[ \Delta d = \text{inv}(K_T) \ast (k - R_E). \]  

Using Equation (2.28) the new values are calculated for the node. The procedure is repeated until:

\[ \Delta d < \text{tolerance}. \]

For the nonlinear steady-state case discussed previously, the analytical solution can be derived. For the same governing Equation (2.9) and the same boundary conditions (2.10) and (2.11), we can obtain the solution for temperature to be of the form:

\[ T(x) = \sqrt{\frac{2}{L_0}} \left( -\frac{g}{2} x^2 + C_1 x + C_2 \right) \quad (a) \]

\[ T(x) = \frac{g_0 L^2}{2k} \left( 1 + \frac{2k}{hL} - \frac{x^2}{L^2} \right) + \frac{g_0 L}{k} \left( 1 + \frac{k}{hL} - \frac{x}{L} \right) + T_\infty \quad (b) \]

where

\[ C_1 = hT_\infty + gL \]

and

\[ C_2 = -2 \frac{P \rho L_0}{L_0} \left( \frac{1}{-2\frac{g}{L_0} x_1 + \frac{2}{L_0} C_1} \right) - \frac{2}{L_0} \left( -\frac{g \rho x_1^2}{2} + C_1 x_1 \right) x_1. \]
Equation (2.35a) is the analytical solution to the nonlinear case where the thermal conductivity is assumed to be a function of temperature (WF). Equation (2.35b) is the analytical solution to the linear case where the thermal conductivity is assumed to be a constant. In most cases, the boundary will be at $x_i=0$. This will simplify the constant $C_2$ in Equation (2.35). The details of Equation (2.35) can be found elsewhere [37].

As can be seen from Figure 2.1, the FEM approximation to Equation (2.9) overlaps the nonlinear analytical solutions, Equation (2.35 (b)) showing the FEM converges to the steady-state answer. When including the analysis of grain size, the temperature at the insulated wall is 420.43 K for $l/d = 1$, while neglecting grain size yields a value of 420.01 K

![1-D steady Temperature Distribution](image)

**Figure 2.1.** Steady-state temperature distribution through a slab of length 1 mm.

The variables are set to: $h=50$ W/(m²K), $g=100$ kW/m³, $T_0=400$ C, epsilon=1.
Figure 2.2 would correspond to a minimum grain size of about 1 nm in a metal such as copper. The calculated temperature at the insulated wall is 440.25 K for a grain size of 1nm, and the corresponding temperature neglecting grain size is 420.13 K (error of +4.79%). The wall thickness is 1 mm (an unrealistic value in thin films used to show large variations in temperature).

![1-D steady Temperature Distribution](image)

**Figure 2.2.** A repeat of Figure 2.1 except the grain size parameter maximum value is 50 here.

**Time Dependence – Newmark’s Method**

Now time \( t \) will be included in the procedure [39], with relaxation time \( \tau \) re-instated in Equation (2.8) for temperature \( T \) represented by row-vector \( d \). Because hyperbolic diffusion is being considered, the second-order time-derivative becomes important. The temperature then is found from the governing equation for \( d = d(t) \) which takes the form:
\[ M\ddot{d} + C\dot{d} + K_T d = F, \quad (2.36) \]

subject to the following initial conditions at \( t=0 \):

\begin{align*}
   d(0) &= T_0 \\
   \dot{d}(0) &= q_0 
\end{align*} \quad (2.37)

A dot over a variable represents differentiation with respect to \( t \). The variable \( F \) here will be similar to \( R_E \) from the previous explanation of the steady-state analysis discussed before,

\[ F = R_E - K \quad . \quad (2.38) \]

Both \( M \) and \( C \) are matrices which are determined from the nodal equations for each element. Their size is \( n \times n \), where \( n \) is the number of elements.

\begin{align*}
   M &= \int N^T \pi N dV \\
   C &= \int N^T \rho c_p N dV 
\end{align*} \quad (2.39)

The iterative procedure will now be described. Complete details for the Newmark method can be found in the literature [39].

\[ Ma_{n+1} + Cv_{n+1} + K_T d_{n+1} = F_{n+1} \quad (2.40) \]

\[ d_{n+1} = d_n + \Delta t v_n + \frac{\Delta t^2}{2} [(1 - 2\beta)a_n + 2\beta a_{n+1}] \quad (2.41) \]

\[ v_{n+1} = v_n + \Delta t [(1 - \gamma)a_n + \gamma a_{n+1}] \quad . \quad (2.42) \]

Generally, the Newmark method uses:

\begin{align*}
   \tilde{d}_{n+1} &= d_n + \Delta t v_n + \frac{\Delta t^2}{2} (1 - 2\beta)a_n \\
   \tilde{v}_{n+1} &= v_n + (1 - \gamma)\Delta t a_n 
\end{align*} \quad (2.43)

To begin the procedure, \( a_0 \) may be calculated from:
\[ M a_0 = F - C v_0 - K d_0 \]  \hspace{1cm} (2.44)

\[ (M + \gamma \Delta t C + \beta \Delta t^2 K_T) a_{n+1} = F_{n+1} - C \bar{v}_{n+1} + K \ddot{a}_{n+1} + \frac{M}{\Delta t^2 \beta} \dot{d} + \frac{C}{\Delta t^2 \gamma} d \ ] \hspace{1cm} (2.45)

Equation (2.45) is known as the "a-form" of Newmark's method. However, the right hand side of (2.45) is written in d-form. Therefore, (2.41) must be substituted into (2.40) and the equation is solved for in terms of \( d_{n+1} \) similar to how Equation (2.34) is solved.

The difference when incorporating time \( t \) is as follows:

\[ J = \frac{M}{\Delta t^2 \gamma} + \frac{C \dot{\gamma}}{\Delta t \gamma} + K_T \]  \hspace{1cm} (2.46)

\[ Q = k - r_E + C \ddot{v} + M \ddot{a} + + \frac{M}{\Delta t^2 \beta} \dot{d} + \frac{C}{\Delta t^2 \gamma} d \]  \hspace{1cm} (2.47)

\[ \Delta d = \text{inv}(J) \star (Q). \]  \hspace{1cm} (2.48)

Notice the similarity between (2.34) and (2.48). Then (2.28) is used to find \( d_{n+1} \).

There are stability conditions, which are discussed elsewhere [39]:

Unconditional:

\[ 2 \beta \geq \gamma \geq \frac{1}{2} \]

Conditional:

\[ \gamma \geq \frac{1}{2} \]

\[ \beta < \frac{\gamma}{2} \]

\[ \omega^h \Delta t \leq \Omega_{\text{crit}} \]

\[ \Omega_{\text{crit}} = \frac{\xi (\gamma - 0.5) + \left[ \frac{\gamma}{2} - \beta + \xi^2 (\gamma - 0.5)^2 \right]^{0.5}}{\gamma/2 - \beta} \]
It should be noted that unconditional stability ($\beta=0.25$, $\gamma=0.5$) was used in all calculations here.

**Radiation**

The inclusion of radiation can expand the analysis. With a modification to $K_T$ and $R_E$ the problem can be solved. Equation (2.11) is extended to include the radiation boundary condition and $T_\infty$ is the ambient temperature as $t \to \infty$:

$$
L_0 T \frac{dT}{dx} \bigg|_{x=L} = h(T_{\infty} - T(x = L)) + \varepsilon \sigma_{SB} \left( T_{\infty}^4 - T^4(x = L) \right)
$$

(2.49)

Here, $\varepsilon$ is the emissivity and $\sigma_{SB}$ is the Stefan-Boltzmann constant. Then $K_T$ and $R_E$ are modified as:

$$
K_T^i = \begin{bmatrix}
\frac{\partial K_1}{\partial T_1} & \frac{\partial K_1}{\partial T_2} & \frac{\partial K_1}{\partial T_3} & \cdots & \frac{\partial K_1}{\partial T_n} \\
\frac{\partial K_2}{\partial T_1} & \frac{\partial K_2}{\partial T_2} & \frac{\partial K_2}{\partial T_3} & \cdots & \frac{\partial K_2}{\partial T_n} \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
\frac{\partial K_n}{\partial T_1} & \frac{\partial K_n}{\partial T_2} & \frac{\partial K_n}{\partial T_3} & \cdots & \frac{\partial K_n}{\partial T_n} 
\end{bmatrix}
$$

$$
R_E = \begin{bmatrix}
\frac{g L}{2L_0} \\
\frac{g L}{2L_0} \\
\vdots \\
\frac{g L}{2L_0}
\end{bmatrix}
$$

(2.50)

No other modifications are needed to make calculations for radiation.

In the calculations section, all results will be based on solving Equation (2.8) subject to the boundary conditions (2.10) and (2.49). The grain size parameter ($l/d$) was varied from 0.001 to 100. For most metals, grain sizes can be as small as 1 nanometer. With a mean free path $l$ of ~40 nm (Copper, Gold, Silver), the $l/d$ ratio might seem unrealistic [1-3, 8]. However, for a metal such as Manganese (mean free path 120 nm), a grain size ratio approaching 100 would correspond to a grain size of 1.2 nm which is
within manufacturing capabilities [18]. Also, in relation to the experimental values used in Chapter 1 of this thesis (Radyne 40kW generator) and a 1 cm³ sample, a realistic value of 4 GW/m³ was used.

**Results and Calculations**

In order to appreciate the results that follow, several comments need to be made regarding the general nature of the hyperbolic differential equation involved in Equations (2.7), (2.8), and (2.36) for temperature \( T \). Of the form \( \ddot{T} + \dot{T} + T = 0 \), this type of equation has two principal parts: \( \dot{T} + T = 0 \) which has an exponential solution; and \( \ddot{T} + T = 0 \) which has a sinusoidal oscillatory solution. When combined, the result is an oscillatory solution that is exponentially damped – a characteristic mentioned for the telegraph equation in Appendix B. That is, the oscillatory solution of one is modulated by the exponential behavior of the other.

One will observe in the forthcoming figures that, depending upon the source term \( g \) (kW/m³ or GW/m³) in these hyperbolic equations, there will exist regions in which the sinusoidal and exponential behavior dominates. All of the solutions begin as damped oscillatory functions but eventually appear to become asymptotically flat as the steady-state temperature is reached, then dominated by the source of heat term \( g \). The colors involved represent increasing/decreasing degrees of grain refinement \( (l/d) \) where \( d \) is grain size parameter (e.g., shown in Figure 2.2). One will also note that fine grain cases (large \( l/d \)) begin as the lower curves on the graphs as a function of time \( t \), but cross over and reverse the order by becoming dominant (the upper curves) when the solution reaches its asymptotic state.
All calculations were made using a standard desktop PC computer and Matlab 7.0 edition student version software. The procedure for the calculations was followed exactly as described in this chapter. The geometry considered was one-dimensional. This can easily be extended to two- and three-dimensions. However, this can significantly increase computational time and for this reason was not attempted. A one-dimensional system required approximately 1 minute of computational time. A two-dimensional system required over 40 minutes and consumed all the virtual memory of the computer. Because of this, no three-dimensional systems were even considered for calculation.

Figure 2.3 and Figure 2.4 show the early time response to the nonlinear hyperbolic heat conduction equation. Figure 2.3 includes the radiative boundary condition while Figure 2.4 does not. With the exception of radiation, all parameters are the same in the two figures. The maximum temperature value in Figure 2.3 is 301.15 while it is 300.33 in Figure 2.4.
Figure 2.3. Time response at the insulated wall for a 10 micron thin film. Initial condition 300 K, \( h = 10 \) W/(m\(^2\)K), \( g = 100 \) kW/m\(^3\), \( T_{\infty} = 600 \) K, \( \tau = 10^{-13} \) s, \( \rho c_p = 10^6 \) J/(m\(^3\)K), epsilon = 1. The curve for \( l/d = 0.001 \) is overlaid by that for 0.01.

Figure 2.4. Time response at the insulated wall for a 10 micron thin film. Initial condition 300 K, \( h = 10 \) W/(m\(^2\)K), \( g = 100 \) kW/m\(^3\), \( T_{\infty} = 600 \) K, \( \tau = 10^{-13} \) s, \( \rho c_p = 10^6 \) J/(m\(^3\)K), epsilon = 0.

The difference is four times greater than the minimum temperature response which is due to the small grained structures (\( l/d > 10 \)) that seem to be unaffected in the early stage of the process. Figure 2.5 differs from Figure 2.3 only in that \( h = 100 \) W/(m\(^2\)K) instead of \( h = 10 \) W/(m\(^2\)K). After the first millisecond, the smaller grain-sized structures (\( l/d > 10 \)) again seem to be fairly unaffected in their temperature response. By increasing the convection coefficient, it is seen that after only 1 millisecond, the temperature is 3 degrees higher than when the lower convection coefficient is used.
Figure 2.5. Time response at the insulated wall for a 10 micron thin film. Initial condition $300 \text{ K}, h = 100 \text{ W/(m}^2\text{K)}, g = 100 \text{ kW/m}^3, T_s = 600 \text{ K}, \tau = 10^{-13} \text{ s}, \rho c_p = 10^6 \text{ J/(m}^3\text{K)}, \epsilon = 1$.

From Figure 2.6, it can be seen that after approximately 5 milliseconds, the rate at which the larger grain size parameter ($l/d > 10$) becomes approximately equal to the rate of the lower grain size parameter temperature profiles.
1-D Unsteady Temperature Response at the Insulated Wall

**Figure 2.6.** Time response at the insulated wall for a 10 micron thin film. Initial condition 300 K, $h = 10$ W/(m$^2$K), $g=100$ kW/m$^3$, $T_x=600$ K, $\tau=10^{-13}$ s, $\rho c_p=10^6$ J/(m$^3$K), epsilon=1.

Figure 2.7 shows the time response after the first 5 hundredths of a second. The variation of grain size parameters can yield a difference of up to 6 degrees at the insulated wall after this time. Based on Figure 2.7 the temperature at this point is 371.5 K when grain size is neglected, and 366 K when the grain size calculation is included. This corresponds to an error of roughly 2% from the expected temperature in Kelvin (6% in Celsius, if that is how the particular experimental equipment processes data).
**Figure 2.7.** Time response at the insulated wall for a 10 micron thin film. Initial condition $300 \text{ K}$, $h = 10 \text{ W/(m}^2\text{K)}$, $g = 100 \text{ kW/m}^3$, $T_w = 600 \text{ K}$, $\tau = 10^{-13} \text{ s}$, $\rho c_p = 10^6 \text{ J/(m}^3\text{K)}$, epsilon=1.
Figure 2.8. Time response at the insulated wall for a 10 micron thin film. Initial condition 300 K, \( h = 10 \text{ W/(m}^2\text{K)} \), \( g = 100 \text{ kW/m}^3 \), \( T_{\infty} = 600 \text{ K} \), \( \tau = 10^{-13} \text{ s} \), \( \rho c_p = 10^6 \text{ J/(m}^3\text{K)} \), \( \epsilon = 1 \).

Figure 2.8 shows the time response after 1 second. It is evident that for the particular conditions the sample has almost asymptotically reached the steady-state value. Because of the scale of the graph (ranging from 300 to 600 K), it is difficult to see any variation in between the small and large grain size parameters. By varying the initial conditions this behavior can be alleviated. In Figure 2.9 the initial temperature is set to 600 K and the ambient temperature is 350 K. This makes it much easier to see the grain size variation. It is important to note that since the parameters have been varied and the initial condition is much closer to the final condition, less time will be needed to reach
steady-state values. Therefore, a direct comparison of Figure 2.9 with previous figures should not be made.

**Figure 2.9.** Time response at the insulated wall for a 10 micron thin film. Initial condition 600 K, \( h = 10 \text{ W/(m}^2\text{K)} \), \( \varphi = 1 \text{ GW/m}^3 \), \( T_x = 350 \text{ K} \), \( \tau = 10^{-13} \text{ s} \), \( \rho c_p = 10^6 \text{ J/(m}^3\text{K)} \), \( \varepsilon = 1 \).

Figure 2.10 has been included to show the significance of the nonlinear radiation boundary condition. The emissivity parameter \( \varepsilon \) was the only value varied between Figure 2.9 and 2.10. As can be seen in Figure 2.10 (\( \varepsilon = 0.1 \)), the temperature after 1 second is 900 K, roughly 300 K more than Figure 2.9 (\( \varepsilon = 1.0 \)). Lowering the value to zero will only amplify the temperature difference more. It is evident that the addition of the nonlinear radiation boundary condition is quite important for problems of this nature.
Figure 2.10. Time response at the insulated wall for a 10 micron thin film. Initial condition $600 \text{ K}$, $h = 10 \text{ W/(m}^2\text{K)}$, $g = 1 \text{ GW/m}^3$, $T_\text{in}=350 \text{ K}$, $\tau = 10^{-13} \text{ s}$, $\rho c_p = 10^6 \text{ J/(m}^3\text{K)}$, epsilon=0.1.

Physically, the relaxation time $\tau$ represents the finite buildup time for the commencement of heat flow. This can be clearly seen in Figures 2.8-2.10. As discussed in Appendix B, $\tau \sim l/(\nu \rho)$, being inversely proportional to velocity $\nu$ and density $\rho$. In the strictest sense $\tau$ is actually a function of temperature, $\tau = \tau(T)$.

Conclusions

The FEM method has been employed to solve the nonlinear time-dependent hyperbolic heat diffusion equation subject to convective and radiative boundary conditions. According to the Wiedemann-Franz law and using the Fuchs-Sondheimer
relation for grain size, it can be seen that when the mean free path is on the same order of
magnitude as the grain size for a conductor, the behavior of heat conduction deviates
from the classical Fourier equation. The addition of the radiation boundary condition was
shown to be necessary. This manipulation of grain size in manufacturing metal films can
be used to optimize thermal properties for specific systems.

References:

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3. Conclusion

The experimental results of the manufacturing of SWCNT-metal-matrix composites were presented in Chapter 1 of this work. Without any metal coating around the nanotubes, the SWCNTs could not survive the rapid heat transfer, high-temperature processing because it would bond with Ti to form TiC. It was this fact that led to the investigation of the variation of thermal properties and the study of relaxation time in Chapter 2. The result was the realization that both the nickel coating and the fast processing time associated with the induction heating method enabled carbon nanotubes to survive the high-temperature processing conditions (> 1950 K). The resulting Ti-SWCNT MMC has never been obtained before this investigation.

The computational analysis in Chapter 2 found the following. The inclusion of the Wiedemann-Franz law and the Fuchs-Sondheimer relation for grain size creating a nonlinear equation showed that the behavior of heat conduction can deviate significantly from the linear hyperbolic heat conduction equation. The FEM method was utilized to solve the nonlinear time-dependent hyperbolic heat diffusion equation subject to convective and radiative boundary conditions. The calculations showed that there can be a large deviation between the linear and nonlinear calculations when grain size is included. The nonlinearities become significantly larger at higher temperatures. When calculations are made for high-temperature situations, numerical methods such as the one presented in this work become mandatory to provide a more accurate description of the physical process.

In conclusion, the introduction of relaxation time linked the model of a finite velocity of thermal propagation with the experimental facts found in the laboratory. Both
the theoretical model and the fast processing time associated with the induction heating method used to create the Ti-SWCNT MMC experimentally were found to be consistent, thus corroborating the rapid heat transfer technique used to create this new composite.
Appendix A – Wiedemann-Franz Law From The Boltzmann Equation

What follows is a derivation of the Wiedemann-Franz law given in Equation (2.2). A detailed explanation of the Boltzmann equation and its numerous applications can be found elsewhere [1]. It will be assumed the reader has a basic understanding of the Boltzmann equation.

A system of randomly moving particles in a medium with a temperature gradient along the x-axis is to be considered. A particle which is scattered, or collides with the medium, has a thermal velocity immediately after the collision with an equilibrium distribution \( f_0(x, T(x)) \) at the collision point.

A particle is moving in a \( \xi \) direction at an angle \( \theta \) with respect to the x-axis and a thermal velocity, \( v \). The projection of the particle in the direction \( \xi \) on the axis is given as:

\[
\Delta x = \Delta \xi \cos \theta
\]  

(A1)

The probability, \( dP \), that a particle will collide with the medium at a distance element \( d\xi \) is proportional to the length \( d\xi \), the density of scattering centers \( n_s \), and their scattering cross section \( \sigma_s \):

\[
dP = -P d\xi \sum n_s \sigma_s = -P d\xi / l
\]  

(A2)

where summation over \( s \) accounts for all centers, and \( l = 1/(\Sigma n_s \sigma_s) \) is the mean free path.

The probability that a particle last collision, before reaching a cross section plane at some \( \xi \), along the element \( d\xi' \), at a position \( \xi'(\xi' < \xi) \) is:

\[
P(\xi')d\xi'/l = e^{(\xi'-\xi)/l} d\xi'/l, \tag{A3}
\]
where \( l \) is the probable distance from which the particle comes (mean free path). The particle velocity distribution, \( v \), at the cross section plane \( \xi \) is obtained by adding local velocity distributions at all the distance elements along the line up to \( \xi \). Each distribution is then multiplied by the probability that the particle comes from \( \xi \), namely, that it has collided for the last time with the medium at that place:

\[
f(\xi, v) = \int_{-\infty}^{\xi} f_0(\xi', v)P(\xi')d\xi'/l
\]

(A4)

where \( v = |v| \) and \( f_0(\xi', v) \) is the local equilibrium distribution at \( \xi' \). If the equilibrium distribution has no significant change along the mean free path \( l \), it is then possible to use the first terms of Taylor series. Velocity changes are a result of external forces acting on the particle. Assuming the force is acting in the \( x \)-direction, the velocity change is then:

\[
f_0(\xi', v) = f_0(\xi, v) + \frac{\partial f_0}{\partial \xi}(\xi' - \xi) + \frac{\partial f_0}{\partial v}(v(\xi') - v(\xi))
\]

(A5)

\[v(\xi')^2 - v(\xi)^2 = 2v(v' - v) = 2a(\xi' - \xi)\cos \theta
\]

(A6)

where \( a \) is the acceleration (\( a = eE/m \)) for an electric field \( E \). Substituting (A6) and (A5) into (A4), integrating over \( \xi' \), and using (A1):

\[
f(x, v, \theta) = f_0(x, v) - l \cos \theta \left( \frac{\partial f_0}{\partial x} + a \frac{\partial f_0}{\partial v} \right)
\]

(A7)

The non-equilibrium distribution given by (A7) is the linear Boltzmann transport equation in a non-traditional form. \( f_0(x, v) \) is the local equilibrium distribution given by Maxwell-Boltzmann or Fermi-Dirac distributions. The medium properties appear through the mean free path \( l \), and external forces through:

\[
\frac{\partial f}{\partial t} + v \nabla_x f + a \nabla_v f = -\frac{(f - f_0)}{\tau},
\]
where the relaxation time is given as $\tau = l/v$, ($l$ being the particle mean free path) and the acceleration is given as $a = eE/m$ for a particle of mass $m$ in an electric field, $E$.

A moving particle with velocity $v$ will cross a plane section at a distance $x$ during a time $\Delta t$ if its distance from that plane is less than $|v|\cos\theta \Delta t$. The particle current through that unit plane section at $x$ is then obtained by summing all velocities from all spatial directions, each velocity being weighed by the distribution probability:

$$J_n = \int f(x, v, \theta)|v|\cos\theta d^3v$$

(A8)

where $d^3v = 2\pi v^2 dv \sin\theta d\theta$. Substitution of (A7) into (A8) yields the particle current:

$$J_n = -\frac{4\pi l}{3} \left(\frac{eE}{m} \int \frac{\partial f_0}{\partial v} v^2 dv + \int \frac{\partial f_0}{\partial x} v^4 dv \right),$$

(A9)

where the $f_0$ contribution in (A7) is zero, and the integral $\int \cos^2 \theta \sin \theta d\theta = 2/3$. The energy of each particle is $(1/2)mv^2$; therefore the energy current will be:

$$J_u = \frac{m}{2} \int f(x, v, \theta)|v|^3 \cos\theta d^3v$$

(A10)

and similarly:

$$J_u = \frac{4\pi l}{3} \left(\frac{eE}{m} \int \frac{\partial f_0}{\partial v} v^4 dv + \int \frac{\partial f_0}{\partial x} v^6 dv \right).$$

(A11)

The currents will now be calculated by applying the Maxwell-Boltzmann distribution:

$$f_0(x, v) = n(x) \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/(2kT)},$$

(A12)

where the local particle density is $n(x)$. In (A12), $n(x)$ is determined by the normalization condition:

$$n = \int_0^\infty 4\pi v^2 f_0 dv.$$
Since, (from (A12)),

$$\frac{\partial f_0}{\partial v} = -\frac{mv}{kT} f_0$$  \hspace{1cm} (A13)

then:

$$J_n = \frac{4\pi l}{3} \left( \frac{eE}{kT} - \frac{d}{dx} \right) \int f_0 v^3 dv$$  \hspace{1cm} (A14)

where the integral equals:

$$\frac{n}{\pi} \left( \frac{kT}{2\pi n} \right)^{1/2} .$$

Therefore, the particle current is given by:

$$J_n = \frac{4l}{3(2\pi n)^{1/2}} \left( \frac{eEn}{(kT)^{1/2}} - \frac{d}{dx} \left( n(kT)^{1/2} \right) \right)$$  \hspace{1cm} (A15)

The energy current by a similar calculation is given as:

$$J_u = \frac{8l}{3(2\pi n)^{1/2}} \left( \frac{eE}{(kT)^{1/2}} - \frac{d}{dx} \left( n(kT)^{3/2} \right) \right)$$  \hspace{1cm} (A16)

The combination of (A15) and (A16) yields:

$$J_\pi = 2kTJ_n - (8l/3) \left( \frac{kT}{2\pi n} \right)^{1/2} n \frac{d(kT)}{dx} .$$  \hspace{1cm} (A17)

The electrical current, $J_q$, is then given by (from (A15)):

$$J_q = eJ_n = \frac{4le^2n}{3(2\pi nT)^{1/2}} \left( E - \frac{k}{2e} \frac{dT}{dx} \right) .$$  \hspace{1cm} (A18)

The transport coefficients are determined directly from (A15)-(A17). The electrical conductivity $\sigma$, defined by:

$$J_q = eJ_n \left( \frac{dn}{dx} = 0, \frac{dT}{dx} = 0 \right) = \sigma E ,$$


65
is then given as:

$$\sigma = \left(4l/3\right)\left(\frac{e^2n}{mkT}\right)^{1/2}.$$  \hspace{1cm} (A19)

The thermal conductivity, defined by

$$J_n \left(J_n = 0\right) = -K \frac{dT}{dx},$$

is given as:

$$K = \left(\frac{8l}{3}\right)\left(\frac{kT}{2\pi n}\right)^{1/2}kn.$$  \hspace{1cm} (A20)

By comparing these coefficients, the Wiedemann-Franz law follows:

$$\frac{K}{\sigma} = 2kT\left(\frac{k}{e}\right)^2.$$  \hspace{1cm} (A21)

References:

Appendix B – Velocity of Propagation: Parabolic versus Hyperbolic Differential Equations

After the historical introduction of Maxwell’s equations, it was realized that electromagnetic radiation (which is involved in heat transfer) could be represented by a hyperbolic wave equation for heat propagation that necessarily travels at the speed of light in vacuum. For the electric field component $E$ of such radiation this equation is

$$\nabla^2 E - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} E = 0 \quad \text{(B1a)}$$

where $c$ is the finite speed of light. Often times this equation is written $\Box^2 E = 0$ where $\Box^2 = \nabla^2 - c^{-2} \partial^2_x$ is known as the D’Lambertian operator. When the electric field is propagating as a wave in a conducting medium, however, (B1a) becomes

$$\nabla^2 E - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} E + \mu \sigma \frac{\partial}{\partial t} E = 0 \quad \text{(B1b)}$$

where $c$ is now the finite velocity of propagation in the medium represented by a conductivity $\sigma$, a permeability $\mu$, and a permittivity $\varepsilon = c^{-2}/\mu$ [1]. A relaxation time $\tau = \varepsilon / \sigma$ is associated with the $\sigma$-term in (B1b) and the propagating wave is exponentially damped, an effect known as the skin depth in metallic conductivity. Equation (B1b) is often referred to as the “telegraph equation” or the “equation of telegraphy.”

In heat transfer theory, on the other hand, there is a serious problem if one attempts to derive a wave equation like (B1) using Fick’s law for diffusive processes. Beginning with the continuity equation for a flux $j$ of a diffusing quantity $\rho$ and a diffusion constant $D$

$$\partial_t \rho(x,t) = - j(x,t) \quad \text{(B2a)}$$
along with Fick’s first law as a constitutive equation

\[ j(x,t) = D \nabla \rho(x,t) \quad , \]  

(B2b)

one takes the gradient of (B2b) and inserts it into (B2a). The result is Fick’s second law

\[ \nabla^2 \rho - D \frac{\partial}{\partial t} \rho = 0 \quad . \]  

(B2c)

Simple comparison of (B2c) with (B1) reveals that the $\Box^2$ or D’Lambertian term has disappeared. Without it there is no longer a wave equation and Fick’s second law amounts to a parabolic equation which implicitly assumes an infinite velocity of propagation – an unacceptable result.

Numerous papers in the literature have addressed this fundamental problem [2]. We will show here one version of the derivation of a hyperbolic heat transfer wave equation usually associated with the name Cattaneo. The derivation follows that given by Nonnenmacher [3] which begins with the Boltzmann transport equation. The latter can be written as:

\[ \left( \frac{\partial}{\partial t} + v \nabla \right) f(x,v,t) = C(f,f) \]  

(B3)

The right-hand side is the collision term and is given as:

\[ C(f,f) = \iiint dv dv' dw' W(vw|v'w')[f(x,v',t)f(x,w',t) - f(x,v,t)f(x,w,t)] \]  

(B3a)

Through simplifications of the collision term, the Boltzmann equation can be written as [4]

\[ \left( \frac{\partial}{\partial t} + \frac{\partial}{\partial x} \right) f_+(x,t) = \nu (f_+^2 - f_-^2) \]  

(B4a)

\[ \left( \frac{\partial}{\partial t} - \frac{\partial}{\partial x} \right) f_-(x,t) = \nu (f_+^2 - f_-^2) \]  

(B4b)
according to the Carleman model. It can can also be written as:

\[
\left( \frac{\partial}{\partial t} + \frac{\partial}{\partial x} \right) f_+(x,t) = \nu (f_+^2 - f_+ f_-)
\]

\[
\left( \frac{\partial}{\partial t} - \frac{\partial}{\partial x} \right) f_-(x,t) = \nu (f_+ f_- - f_-^2)
\]

according to the McKean model [5].

Here, we have used the short hand notation for the distribution functions:

\[ f_\pm = f_\pm (x,t) = f(v_\pm, x, t) = f(\pm 1, x, t) \]

In terms of discrete velocity distribution functions \( f_+ \) and \( f_- \) the particle density \( \rho (x,t) \) and particle flux \( j(x,t) \) are given respectively, by replacing integration by summation over the two discrete velocities \( v = v_+ = 1 \) and \( v = v_- = -1 \):

\[
\rho (x,t) = \int dv f (v, x, t) = f_+ + f_-
\]

\[
j(x,t) = \int dv vf (v, x, t) = f_+ - f_-
\]

First we observe that both models conserve the particle number. Adding (B4a) and (B4b) together we obtain:

\[
\frac{\partial}{\partial t} (f_+ + f_-) + \frac{\partial}{\partial x} (f_+ - f_-) = 0
\]

Using now (B6a) and (B6b), we finally get the one-dimensional equation of continuity

\[
\frac{\partial \rho}{\partial t} + \frac{\partial j}{\partial x} = 0
\]

McKean’s model, by adding (B5a) and (B5b) together, yields the same result.

In order to find the constitutive equation we subtract (B4b) from (B4a) leading to

\[
\frac{\partial}{\partial t} (f_+ - f_-) + \frac{\partial}{\partial x} (f_+ + f_-) = 2\nu (f_+^2 - f_-^2) = -2\nu (f_+ + f_-)(f_+ - f_-)
\]

69
Again using (B6a) and (B6b) one gets for the Carleman model the following non-linear constitutive equation:

$$\frac{\partial j}{\partial t} + \frac{\partial \rho}{\partial x} = -2\nu \rho(x,t) j(x,t)$$  \hspace{1cm} (B8)

And similarly for the McKean model one obtains:

$$\frac{\partial j}{\partial t} + \frac{\partial \rho}{\partial x} = -\nu j(x,t)[\rho(x,t) - j(x,t)]$$  \hspace{1cm} (B9)

After the right and sides of (B8) or (B9) are made linear around an equilibrium density $\rho_0$,

$$\rho(x,t) = \rho_0 + \rho_1(x,t)$$

and an equilibrium flux $j_0=0$

$$j(x,t) = j_0 + j_1(x,t) = j_1(x,t)$$

where $j_1$ and $\rho_1$ are deviations for their equilibrium values, we obtain by neglecting nonlinear terms the linearized version of (B8)

$$\frac{\partial j_1}{\partial t} + \frac{\partial \rho_1}{\partial x} = -2\nu \rho_0 j_1(x,t)$$

More explicitly, one has

$$\left(1 + \frac{1}{2\nu \rho_0} \frac{\partial}{\partial t}\right) j_1(x,t) = -\frac{1}{2\nu \rho_0} \frac{\partial \rho_1}{\partial x}$$  \hspace{1cm} (B10)

Linearizing (B9) yields:

$$\left(1 + \frac{1}{\nu \rho_0} \frac{\partial}{\partial t}\right) j_1(x,t) = -\frac{1}{\nu \rho_0} \frac{\partial \rho_1}{\partial x}$$  \hspace{1cm} (B11)

Both results represent a Cattaneo-type constitutive law. The parameter $1/(2\nu \rho_0)$ or $1/(\nu \rho_0)$ can be associated with the relaxation-time parameter $\tau$, depending on the model under consideration. By introducing $\tau$ into the constitutive equation, a satisfactory hyperbolic
heat transfer wave equation of the type in Equation (2.7) of the text follows. A comparison of (2.7) with (B1b) illustrates the result.

References: