A COMPUTATIONAL STUDY ON EXTENSION OF NON-CONTACT MODULATION CALORIMETRY

Xiao Ye
University of Massachusetts - Amherst

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A COMPUTATIONAL STUDY ON EXTENSION OF NON-CONTACT MODULATION CALORIMETRY

A Dissertation Presented
by
XIAO YE

Submitted to the Graduate School of the University of Massachusetts Amherst in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

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Mechanical and Industrial Engineering
A COMPUTATIONAL STUDY ON EXTENSION OF
NON-CONTACT MODULATION CALORIMETRY

A Dissertation Presented
by
XIAO YE

Approved as to style and content by:

______________________________
Robert W. Hyers, Chair

______________________________
David P. Schmidt, Member

______________________________
David M. Ford, Member

______________________________
Donald L. Fisher, Department Head
Mechanical and Industrial Engineering
ACKNOWLEDGMENTS

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ABSTRACT

A COMPUTATIONAL STUDY ON EXTENSION OF NON-CONTACT MODULATION CALORIMETRY

MAY 2015

XIAO YE
B.S., SOUTHEAST UNIVERSITY
M.S., UNIVERSITY OF MASSACHUSETTS, AMHERST
Ph.D., UNIVERSITY OF MASSACHUSETTS AMHERST

Directed by: Professor Robert W. Hyers

Accurate thermophysical properties of high temperature metallic liquids are important for both industrial applications and scientific research. For the former, as predictive numerical simulations play an increasingly important role in pivotal industries, such as casting, welding and sintering, the lack of precise thermophysical properties, especially at high temperatures, hamper their further applications. On the other hand, from the stand point of basic metals physics, being able to measure calorimetric properties of liquid metallic alloys allows the calculation of their thermodynamic functions, which facilitates the study of solidification kinetics of quasicrystals.

This research focuses mainly on measuring properties that governs heat and fluid flow, namely specific heat and thermal conductivity. Conventional techniques generally require test materials, whether solid or liquid, in direct contact with a fastener or
a container, which limits the application of these methods at high temperatures due to elevated thermal reactivity and also intensified heat and mass transfer. To overcome these drawbacks, a non-contact modulation calorimetry has been developed in the 1990s. Specifically, a spherical sample, usually smaller than 10mm in diameter, is levitated using electromagnetic levitation (EML) in a vacuum or gas cooling atmosphere. Thermophysical properties are extracted by analyzing the temperature response on the surface of the sample induced by modulated heating input. This method has been proved relevant for the measurements of specific heat but is limited in thermal conductivity measurements for liquid samples because of the influence of forced convection.

In this study, a two-dimensional axisymmetric model is developed in COMSOL Multiphysics. Using magnetohydrodynamic simulation, firstly, the relevance of the operational principles of this method based on coupled heat flow model developed by Wunderlich, et al., is examined at both reported and unknown parameter range for specific heat measurements. Secondly, systematic error of thermal conductivity measurements using empirical equations in EML based modulation calorimetry is evaluated. Lastly, the possibility of combining numerical simulations and experiments to measure thermal conductivity is explored.
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CHAPTER 1
INTRODUCTION

1.1 Motivation

Accurate thermophysical properties of high temperature metallic liquids are invaluable to both industrial applications and scientific research. The fundamental of materials engineering dictates that properties of a material is a direct result of its processing and structure. Thus, in order to keep up with demanding requirements imposed on high performance materials in cutting-edge applications, such as turbine blades of land-based power plants, high efficiency engines, supermetals, high-performance magnets and etc.[29], it is necessary to have more precise control over processing and thus structure. This challenge can be best tackled through quantitative numerical simulation (Figure 1.2). Nowadays, this method has been adopted in various different industries, such as casting (Figure 1.1), welding, sintering and so on [7].

To obtain plausible simulation results, reliable thermophysical properties are a must. While at low temperatures, thermophysical properties can be measured fairly easy and with high accuracy, the same task can be formidable at high temperatures due to various practical problems, such as chemical reactions between test specimen and container or reduced accuracy of the measurement due to intensified heat transfer. As such, critical thermophysical properties at this regime are scarce or oftentimes simply not available [46, 39].

On the other hand, from the stand point of basic metal physics, accurate thermophysical properties of metallic melts allows study of solidification kinetics of qua-
Figure 1.1. Surveyed significance of different thermophysical properties in U.K metal production business [30]

Figure 1.2. Numerical simulation of internal temperature distribution of a car engine block using MAGMASOFT
sicrystalline from undercooled liquid phase. Quasicrystals were firstly discovered in 1984 by Shectman, et al. [81]. They have a unique structure that displays medium to long range ordering while lacking the periodicity of common crystalline phases (Figure 1.3).

![Figure 1.3.](image)

Figure 1.3. (a) shows a local fivefold non-translational symmetrical unit [50]. (b) is a simple icosahedron consisting of Titanium (Ti), Zirconium (Zr) and Nickel (Ni) atoms [38].

This very structure, namely icosahedral ordering, has actually been hypothesized by Frank in 1952 where he proposed that liquids can be supercooled and held in undercooled liquid state due to the large thermal dynamic barrier required for the transition from preferential short range icosahedral ordering to stable crystalline lattice [33]. In 2003, Kelton, et al., confirmed this hypothesis and shows that the degree of icosahedral ordering is proportional to the undercooling [51]. Since this internal structural change can be correlated to the changes in thermophysical properties and control over the degree of ordering is vital to the formation of quasicrystals, being able to accurately monitor thermophysical properties are of important to quasicrystalline studies.

Generally speaking, thermophysical properties include specific heat capacity, heat of fusion, thermal conductivity, density, surface tension, viscosity, thermal expansion coefficient, melting range, electrical resistivity, emissivity and so on. Those of interest for current research are the caloric quantities: specific heat capacity ($c_p$) which
characterize the ability for a certain material to contain heat and thermal conductivity (k) which describes the ability of a material to conduct heat. In the following, conventional methods for \( c_p \) and k measurements are briefly reviewed with pros and cons of individual methods discussed.

1.2 Specific Heat Capacity Measurements

Specific heat capacity \( (c_p) \) is a fundamental thermophysical property which measures the amount of heat required to change the temperature of unit mass of a substance by one degree. It is defined as the following,

\[
c_p = \frac{Q}{m\Delta T}
\]  

(1.1)

where \( Q \) is the amount of heat that results in the temperature change \( \Delta T \) in a substance with mass \( m \). As the definition suggests, \( c_p \) can be most conveniently measured by measuring \( Q \) and \( \Delta T \) when a specimen experienced a controlled temperature change. Based on this idea, numerous methods have been developed. In this section, five major established techniques for measuring \( c_p \) will be discussed.

1.2.1 Differential Thermal Analysis

Differential thermal analysis (DTA) is a technique that measures thermophysical properties of test materials by monitoring the temperature difference between a sample and a reference standard that undergoes the same thermal cycles [61].

Measuring \( c_p \) with DTA (Figure 1.4) consists of three steps. Firstly, run DTA apparatus with empty sample container and empty reference container and record the temperature difference to produce a zero baseline \( S_B \). If the sample and reference containers were thermally identical, the baseline should be perfectly zero. However, this is rarely the case due thermal asymmetry in the instrument and is not required for evaluation of \( c_p \). Secondly, put a standard reference material with known mass \( m_R \)
and \( c_p(R) \) in the sample container and run under the same heating rate as the first run to generate a reference signal \( S_R \). Finally, replace the reference with a unknown \( c_p(S) \) sample but known mass \( m_S \) and run under the same heating rate to generate a sample signal \( S_S \). Note that all three signals are recorded as a function of temperature [83, 14] and the reference container is empty all the time.

When the experiment is deliberately designed, then the temperature difference between the sample container and the reference container should result solely from the thermal load represented by the specimen and reference, respectively. Then, the specific heat \( c_p \) of the unknown material can be evaluated with the following relationship,

\[
\frac{(S_S - S_B)}{(S_R - S_B)} = \frac{m_S \cdot c_p(S)}{m_R \cdot c_p(R)} \tag{1.2}
\]

Detailed description on measuring \( c_p \) with DTA can be found elsewhere [79, 15].

The major advantages of using DTA are the well-established theory and commercial available apparatus. Due to the structure of the instrument, speedy measurements are possible because of the ease loading. This technique has fairly high accuracy and resolution with a capability to deal with small samples over wide range of tempera-
Some disadvantages associated with this method are that firstly, apparatus need to be calibrated before use. Secondly, packing, size distribution of the test sample could potentially affect the measurement. For example, flat specimens can have a better thermal contact with the container than odd-shaped specimens and thus thermal equilibrium can be obtained easier with consequently more accurate measurement of the differential temperature signal. Thirdly, different heating rate adopted in the method can affect the resulted DTA curve and cause trouble in the interpretation of the experimental signal. Finally, precautions for chemical reactions should be used before the design of the experiment, especially at high temperatures [83].

1.2.2 Differential Scanning Calorimetry

As a successor, differential scanning calorimetry (DSC) resembles DTA in design, operation, result curves and applications. However in fact, they are two fundamentally different thermal analysis techniques. The most critical difference lies in that DSC measures individually the energy transferred to the sample and the reference while in DTA energy is related to the differential temperature signal through calibration.
There are two basic types of DSCs: the heat flux DSC (HF-DSC) and power compensation DSC (PC-DSC). The former is effectively the same as quantitative DTA [15, 10]. Figure 1.6 shows a schematic of HF-DSC with disk type measuring system. Note that in quantitative DTA, the heating block that surrounds the sample and the reference containers acts the same as the direct thermal link (the heat-flux plate) in HF-DSC.

![Figure 1.6. Schematic of Heat Flux DSC. [69]](image)

PC-DSC (Figure 1.7) is the true DSC in that steady-state heating is provided by individual heaters to maintain the temperature equilibrium between the specimen and the reference.

Using PC-DSC to measure \( c_p \) entails the same three procedures as DTAs. And the data curve is also similar (Figure 1.8).

Specifically, with the sample/reference introduced, the baseline of PC-DSC will be shifted towards the endothermic direction due to the extra thermal load. If the instrument was well conditioned and same heating rate was used for each run, the
Figure 1.7. Schematic of Power Compensation DSC [69].

Figure 1.8. Measuring $c_p$ with Power Compensation DSC [15].
displacement (D) of the sample/reference line which represents the compensating heat flux (\( \frac{dq}{dt} \) in the figure) should be proportional to the heat capacity of the sample or the reference. Then, assuming there is no first order phase transition, \( c_p \) can be evaluated with a similar relation as in DTA:

\[
\frac{D_S}{D_R} = \frac{m_S \cdot c_p(S)}{m_R \cdot c_p(R)} \tag{1.3}
\]

Again, subscripts S and R denote the sample and the reference respectively.

As a well-established technique, DSC generally shares the same merits as DTAs. However, there are still some inherent defects that cannot be overcome. Firstly, requirements for better sensitivity and resolution conflicts with each other. The former demands larger sample size and heating rate while the later necessitates the opposite. Secondly, \( c_p \) cannot be measured under isothermal conditions, which imposes a difficulty for measuring \( c_p \) near transition temperatures. Thirdly, first order transition cannot be studied and unfortunately that is exactly the process we want to study in the future.

### 1.2.3 Modulation Calorimetry

Modulation calorimetry (MC) measures thermophysical properties of materials by analyzing the oscillatory temperature response of test sample induced by periodically modulated heating. The basic principle of MC was discovered a century ago by Corbino [21, 22]. However, most researchers were not familiar this method until the systematic rediscovery by Sullivan and Seidel [88, 89]. Table 1.1 lists some important milestones over the development of MC [35]. Due to its high sensitivity and temperature resolution as well as wide applicable range with respect to temperature and pressure [55], MC has gain wide popularity in distinct fields [25, 74, 11, 1].

Generally, in MC, the modulated heating can be expresses as,

\[
T(t) = T_0 + qt + T_\omega \sin(\omega t) \tag{1.4}
\]
Table 1.1. Important milestones of the development of modulation calorimetry [35]

<table>
<thead>
<tr>
<th>Year</th>
<th>Subject</th>
<th>Authors</th>
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<tr>
<td>1910</td>
<td>General theory of principle of $3\omega$ method</td>
<td>Corbino</td>
</tr>
<tr>
<td>1911</td>
<td>First application of $3\omega$ principle</td>
<td>Corbino</td>
</tr>
<tr>
<td>1922</td>
<td>Use of thermionic current oscillations</td>
<td>Smith and Bigler</td>
</tr>
<tr>
<td>1960</td>
<td>Development of $3\omega$ method</td>
<td>Rosenthal</td>
</tr>
<tr>
<td>1962</td>
<td>Bridge circuit for wire sample at $T &gt; 1200^\circ C$</td>
<td>Kraftmakher</td>
</tr>
<tr>
<td>1963</td>
<td>Application of photodetectors</td>
<td>Loewenthal</td>
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<tr>
<td>1965</td>
<td>Heating by electron bombardment</td>
<td>Filipov and Yurchak</td>
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<tr>
<td>1966</td>
<td>Modulated resistive-heating and low-T experiments</td>
<td>Sullivan and Seidel</td>
</tr>
<tr>
<td>1967</td>
<td>Modulated light-heating</td>
<td>Handler et al.</td>
</tr>
<tr>
<td>1974</td>
<td>High-pressure calorimetry</td>
<td>Bonilla and Garland</td>
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<tr>
<td>1979</td>
<td>Improvement of light-modulated method, measuring of thermal diffusion coefficient</td>
<td>Hatta/Ikeda and Ishikawa</td>
</tr>
<tr>
<td>1981</td>
<td>High-frequency relaxation ($&gt; 10^5$ Hz)</td>
<td>Kraftmakher</td>
</tr>
<tr>
<td>1986</td>
<td>Specific heat spectrometer</td>
<td>Birge/Dixon</td>
</tr>
<tr>
<td>1989</td>
<td>Ultra-small sample measurement ($&lt; 100\mu g$)</td>
<td>Graebner/Inderhees</td>
</tr>
<tr>
<td>1991</td>
<td>Modulated temperature DSC (MT-DSC)</td>
<td>Reading, Elliot and Hill</td>
</tr>
</tbody>
</table>

where, $T(t)$ is the programmed heating, $T_0$ is the starting temperature, $q$ is a constant, $T_w$ and $\omega$ are the amplitude and angular frequency of the imposed temperature modulation. The underlying heating rate consists of a constant part and a fluctuating part.

$$\frac{dT}{dt} = q + \omega T_w \cos(\omega t)$$ (1.5)

The governing heat balance equation for the test specimen can be written as:

$$\frac{dQ}{dt} = mc_p \frac{dT}{dt} + f(T, t)$$ (1.6)

which states that the total heat flow ($\frac{dQ}{dt}$) equals the internal energy change of the sample (with mass $m$) and the heat absorbed/released by any kinetic processes during the analysis $f(T, t)$.

Substitute the sinusoidal heating rate into the heat balance equation 1.6,\n
$$\frac{dQ}{dt} = mc_p[q + \omega T_w \sin(\omega t + \phi)] + f(T, t)$$ (1.7)

Obviously, the observed heatflow signal should also be periodic with amplitude $mc_p \omega T_w$. 10
Figure 1.9. Illustration of the temperature programme of modulated temperature DSC: a sinusoidal modulation was superimposed on to a constant ramp. [104]

Figure 1.10. Typical MT DSC data for a polymer from temperature below glass transition to above melting temperature. Phase lag obtained by analyzing the separated modulation signal with a Fourier transform procedure [73].
Figure 1.10 shows raw data of modulated-temperature differential scanning calorimetry (MT-DSC), which is a representative MC, for a polymer from temperature below glass transition to above melting temperature. The top curve is the total heat flow signal. Averaging the raw data over several periods would give a signal without modulation which is in fact equivalent to conventional DSC signal. Then, the modulation part of the signal can be obtained by subtracting this average signal from the total signal. Equating the amplitude of the modulation amplitude $A(t)$ to the analytical solution in equation 1.7 gives,

$$c_p = \frac{A(t)}{m \omega T_w}$$  \hspace{1cm} (1.8)

Compared to traditional DSCs and DTAs, MC excels in several facets. Firstly, it enables $c_p$ measurements in a single run. Secondly, it has a much better sensitivity and accuracy than traditional DSCs. Last and most importantly, since the heat flow signal from kinetic processes $f(T, t)$ can be discerned from the total signal, MC is capable of studying processes that are not amendable to its predecessors, such as chemical reactions, enthalpy relaxation, evaporation, crystallization, decomposition and cure.

1.2.4 High Temperature Calorimetry

Given that potential quasicrystal forming materials are transition metals (Ti, Zr) based binary or multicomponent alloys having melting temperatures generally higher than 1000°C, calorimetry with high temperature (HT) capability are needed. Drop calorimetry, adiabatic calorimetry and pulse calorimetry are some common options.

Drop calorimetry (Figure 1.11 (a)) is the method with which the majority of current HT $c_p$ data in the literature was obtained [80]. Typically small samples preheated to different known temperatures were dropped into the cavity of a large insulated calorimeter block. Under the idea case, the temperature increase of the block after reaching equilibrium should be proportional the sensible heat stored in
the test specimen. With enough repetition, a sensible heat versus temperature curve for the test material can be produced and the slope of the curve is $c_p$ of the material at given temperatures.

Figure 1.11 (b) is a schematic of an adiabatic calorimeter. The specimen is heated by an electrical heater. When the temperature increase is small, by measuring the current and voltage through the electrical leads, the energy input and thus $c_p$ can be calculated directly. The key to this method is to minimize the radiative heat loss from the calorimeter to the environment. However, this gets increasingly harder for higher temperatures.

A pulse calorimeter is shown in Figure 1.11 (c). The idea is simple, which is to reduce the unwanted heat exchange between sample and environment by shorten the time of the measurements. Typically, in pulse calorimetry, a known amount of heat is provided by electric current or by electron bombardment to the preheated sample. The resulting temperature increment, usually small, is measured. Then, dividing the input energy by the temperature increase gives $c_p$. At high temperature, additional calibrations with sample of known specific heat can be performed to estimated heat loss through radiation. This method is applicable only to conducting materials.

### 1.3 Thermal Conductivity Measurements

Naturally, there are three mechanisms for heat transfer: conduction, convection and radiation. Thermal conductivity, denoted with $k$, characterizes the ability of a material to conduct heat through conduction. For an isotropic material at steady state condition, $k$ can be derived from the Fourier’s law:

$$k = \frac{Q/A}{\Delta T/\Delta L}$$  \hspace{1cm} (1.9)

where, $Q$ is the amount of the heat passing through a cross-section $A$. $\Delta T$ is the resulting temperature difference over length $\Delta L$. 

13
Figure 1.11. Image (a) is a drop calorimeter with A,B,C heaters, D hollow alumina beads, E alumina supporting tube, F protecting tube, G calorimeter tube, H refractory bricks, I ceramics, J refractory plug, K thermocouples [48]. Image (b) is an adiabatic calorimeter with A specimen, B adiabatic enclosure, C vacuum furnace, D vacuum chamber, E&G thermocouple, F sheath [80]. Image (c) is a pulse calorimeter [56].
Based on the inherent time scales, common $k$ measuring techniques can be divided into two categories: steady state methods and transient methods. The former exploits equation 1.9. And the key is to minimize heat transfer through the other two mechanisms. However, this is hard at high temperature and for liquid samples. Transient methods alleviates this problem by shorten the experimental duration. But still, $k$ of high temperature materials, especially liquids measured with currently available transient techniques are not without doubt.

1.3.1 Guarded Hot Plate Method

Guarded hot plate (GHP) method is a well-established steady state method which has been included into the annual book of ASTM standards [2]. In this method, a near steady-state axial heat flow is realized with carefully designed apparatus. Figure 1.12 is a schematic of conventional symmetrically arranged guarded hot plate apparatus [59] where the heating assembly (the hot plate) is sandwiched by two identical slab shaped specimens.

![Figure 1.12. Schematic of guarded hot-plate method for the measuring of thermal conductivity [59].](image)

The heating assembly consists of a metered plate and co-axial primary guard plate. A PID feedback control system is used to maintain the same temperature of the two parts to minimize radial temperature gradient, and thus ensure no radial heat flow.
Edge insulation and guards are used to create an adiabatic environment. Though the true adiabatic condition can hardly be achieved, but as long as the aspect ratio of the specimen is high, the flow near the center of the heating assembly would be pure axial [83]. The cold plates function as isothermal sinks to ensure the same temperature drops over the two specimens. After a long enough period that the steady-state is reached, 

\[ Q = \frac{KA\Delta T}{L} + \frac{KA\Delta T}{L} \]  

(1.10)

where, \( Q \) is the heat flow rate measured within the metered plate, \( \Delta T \) is the temperature drop across the specimen and \( L \) is the thickness of the sample. \( A \) is the area of the metered plate. So, thermal conductivity \( k \) can be calculated as,

\[ k = \frac{QL}{2A\Delta T} \]  

(1.11)

### 1.3.2 Radial Heat Flow Method

Similar to GHP method, radial heat flow method also measures thermal conductivity by monitoring one-dimensional steady state heat flow. The tested specimen in this method is manufactured into a annular cylindrical shape with inner radii \( r_i \), outer radii \( r_o \) and length \( L \)(Figure 1.13).

In the ideal case, a constant amount of heat \( (Q) \) flows steadily from the inner surface with temperature \( (T_i) \) to the outer surface at \( T_o \). At any intermediate cylindrical surface with radii \( r \),

\[ Q = -kA_r \frac{dT}{dr} \]  

(1.12)

where, \( A_r = 2\pi rL \) is the area of the surface with radii \( r \). Rearrange,

\[ \frac{dr}{r} = -\frac{K2\pi L}{Q}dT \]  

(1.13)
Integrate both side from $r_i$ to $r_o$ and $T_i$ to $T_o$ respectively gives,

$$\ln \frac{r_o}{r_i} = -\frac{K2\pi L}{Q}(T_o - T_i)$$ \hspace{1cm} (1.14)

Then,

$$k = \frac{Q\ln{r_o/r_i}}{2\pi L(T_i - T_o)}$$ \hspace{1cm} (1.15)

Figure 1.14 is a thermal conductivity measuring apparatus based on radial heat flow methods. Note that in order to ensure unidirectional heat flow which is the key to this method, low thermal conductivity casing made of alumina or mullite for the center electric heater as well as insulation materials are used to ensure temperature uniformity on the inside and outside surfaces of the sample. Besides, External heating wires are separated into individually controllable zones to minimize temperature gradient along the axial direction and thus minimize lateral heat flow. In practice, the heat dissipated through the heater is calculated by measuring the current and voltage drop and temperature is measured by embedded thermocouples [83].
Both GHP method and Radial heat flow method are steady state methods. The principal advantage provided by these methods is the high accuracy. However, at elevated temperatures, the measurement accuracy deteriorates due to unwanted heat transfer through radiation/convection and expansion of the geometric quantities used in the k equation. Nevertheless, should a steady state method needed for specific HT application, radial heat flow method is more preferred because of the internal heating design which can reduce radiation loss. Currently, HT GHP apparatus can only be used under a maximum temperature of 800°C [96], while modified radial heat flow method can hit around 1500°C [52].

1.3.3 Hot Wire Method

Hot wire method is a transient method. Figure 1.15 (a) shows a schematic of a hot wire cell assembly. The mathematical model for this method considers an infinite long line heating wire (radius r) surrounded by a homogeneous test specimen. Starting at an equilibrium temperature $T_0$, a constant amount of heat (Q) is dissipated from the wire to heat up the specimen. Given the boundary conditions that the temperature
of the specimen far away from the wire remains \( T_0 \) and the heat flow condition near the surface of wire is close to pure radial, the temperature increase at the surface of wire can be approximated as,

\[
\Delta T(t) = \frac{Q}{4\pi k} \ln \frac{4\alpha t}{r^2C}
\]  

(1.16)

where, \( \alpha \) is the thermal diffusivity of the specimen defined

\[
\alpha = \frac{k}{\rho c_p}
\]  

(1.17)

with \( \rho \) and \( c_p \) are density and specific heat. Constant \( C = e^\gamma = 1.781 \) where \( \gamma = 0.5772 \) is the Euler’s constant [37].

![Diagram](image)

**Figure 1.15.** (a) is a schematic of a hot wire apparatus [94]. (b) is the contrast between theoretical and actual temperature time curve [24].

This approximation only applies when the wire is sufficiently thin and experiment time is long enough so that \( r^2/4\alpha t \ll 1 \). Then, thermal conductivity can be evaluated based on the slope (S) of the temperature versus log-time plot of \( \Delta T(t) \).
\[ S = \frac{Q}{4\pi k} \]  \hspace{1cm} (1.18)

Rearrange,
\[ k = \frac{Q}{4\pi S} \]  \hspace{1cm} (1.19)

In fact, the real temperature time curve is not strictly straight from \( t = 0 \) s to the end because of the limited applicability of the assumption in the deduction of the ideal model. Therefore, only the linear portion of the curve is used to calculate \( k \) (Figure 1.15 (b)).

Historically, hot wire method is developed to measure \( k \) of liquids and gases. Hence, compared to steady state methods, it is more suitable for investigations of liquids. Besides, the transient feature of this method makes fast measurement possible whereas stable unidirectional flow could take several days to establish in steady state methods. The major disadvantages associated with this method are firstly the limited temperature range. As temperature increases, the coating surrounds the wire could be less effective as in low temperature and causes current leaks which results into an erroneous \( Q \). Secondly, the mismatch of the thermal expansion of the coating and the specimen can cause spalling. Lastly, compatibility issues can arise due to elevated chemical reactivity of both coatings and specimen.

1.3.4 Flash Method

In this method, a short pulse of high intensity energy in terms of flash, laser or electron bombardment, is casted to the front surface of a disc shaped sample (Figure 1.16). The temperature response on the back of the sample is continuously recorded. Due to definite heat loss, the temperature curve will reach a maximum temperature at time \( t_{\text{max}} \). The thermal transport property directly measured with this method is actually thermal diffusivity \( (\alpha) \) [70],
\[ \alpha = 0.1388 \frac{L^2}{t_{0.5}} \]  \hspace{1cm} (1.20)
where, \( L \) is the thickness of the sample and \( t_{0.5} \) is the time that the rear-surface temperature reaches half of its maximum value \( T_{\text{max}} \). If the density and specific heat at the experimental temperature was known, thermal conductivity can be obtained according to equation 1.17,

\[
k = \alpha \rho c_p
\]  

(1.21)

In practice, more complex versions of this method using temperature values at \( t_x \), where \( x = \frac{T}{T_{\text{max}}} \neq 0.5 \) are also available [60].

![Figure 1.16. Skematic of the principle of laser flash method](image)

As a well-proven method, flash method is more advantageous compared to other \( k \) measuring methods due to its distinct features in experimental design and data manipulation. Firstly, measurement of this method is fast so that almost instantaneous results can be obtained. This feature is particular useful when applied to liquids because the whole measurement can be done before the onset of convection. Secondly, unlike other methods, accurate determination of the amount of heat flux is not needed which makes this method very convenient. Thirdly, in practice, the temperature signal on the rear face of the specimen is usually diagnosed with a remote pyrometer, so there is less contact of the test specimen with external environment than other methods. This allows flash method to be applied at very high temperature regime.
Despite all these merits, flash method is not without weaknesses. The above analytical solution for thermal diffusivity comes with the assumption that the radiation energy from the heat source was absorbed on the front surface of specimen uniformly and propagates one-dimensionally toward the back of the specimen. In order to make sure good absorption rate on the front surface, thin coating of carbon-black paint is usually applied in the experiment and this measure is sometimes not compatible with certain materials, such as iron, which has high carbon solubility. Moreover, though temperature probe and the test specimen is separated, flash method is still essentially a contact method because of the need for containment of the specimen. Nevertheless, flash method is still now the first choice for high temperature applications [83].

1.3.5 Modulation Methods

The idea of utilizing modulated heating can also be applied in k measurement. Depending on the need for \( c_p \), there are calorimetric methods and non-calorimetric methods. The former are extensions of modulation calorimetry while the later should better be addressed as thermal wave methods

- Modulation Calrimetry

Measuring \( k \) with MT-DSC was initially proposed by Marcus and Reading in 1994 and has now been formalized in ASTM standards[63, 84]. It entails conducting MT-DSC experiments on two specimens, one small one large, made of the same material machined into a right circular cylinder shape or simply a rod. For the small specimen, during the experiment the temperature profile within can be assumed to be uniform and thus specific heat capacity \( c_p \) (J/gK) of the material can be accurately measured equivalent to conventional DSC methods. Then, identical modulated heating programme is applied on one end of the cylindrical specimen with length \( L \) (mm), thickness \( d \) (mm) and mass \( m \) (mg) and an apparent heat capacity of the sample C
(mJ/°C) can be obtained. Due to the largeness of the dimension of the specimen, temperature distribution in the thick specimen would not be uniform and the apparent heat capacity would be lower than the case of uniform temperature. Marcus, et al., has determined that C is proportional to the square root of thermal conductivity of the test specimen [64]. k is thus determined with,

\[
k = \frac{8LC^2}{c_pmd^2B}
\]

where B is the period of the temperature modulation. Detailed analytical treatment of this method can be found in reference [8].

- **Thermal Wave Methods**

  In thermal wave methods, generally an periodic temperature boundary was imposed to the test specimen and the thermal response was recorded for the evaluation of k. And usually k is measured indirectly by measuring thermal diffusivity \(\alpha\). Currently, various thermal wave methods exist[9]. The major difference between different versions is the geometry of the test sample and subsequently different analytical solutions to the abstract mathematical model as well as corresponding expression for evaluating k [18, 62, 52].

**1.3.6 Application to Liquids**

In reality, three natural heat transfer mechanisms happen simultaneously. So, in order to accurately measure k which describes the heat transferring ability of a certain material through only conduction, it is important to distinguish the effect of other two mechanisms.

For solids, firstly of all, there is no heat transfer through convection. On the other hand, at low/intermediate temperature, radiative heat loss can be safely ignored. While at higher temperatures, due to its proportionality to the fourth order
of temperature and surface area, radiative heat loss can be evaluated rather simply as long as the test specimen has a regular shape.

However, problem gets complicated for liquids. Researchers have shown that convection can happen as soon as just 1s after a temperature gradient is applied [67]. Therefore, minimizing convection or quantitatively separate convection in measured apparent k become the greatest concern when these method are applied to liquid phase, especially at high temperatures.

Generally, steady state methods are seldom applied to studying k of liquids because convection effect is hard to be ruled out or characterized in the routinely long experiments. Nevertheless, due to simplicity and well established measuring procedures, there still have been attempts with steady state methods on fluids: GHP method [93] and radial heat flow methods [82, 45, 68]. Transient methods are more preferred for liquids because of fast measurement. Hot wire method has been used extensively in studying the heat transfer enhancement of nanofluids but is limited at moderate temperatures [3, 72, 106, 58, 71]. Flash methods is more suitable for high temperature investigations, especially for liquid metals and alloys [49, 86, 85, 27]. Modulation methods again are generally used in low temperature applications, such as in polymer science [48, 78, 17, 20, 90, 19, 18, 94].

1.4 Non-Contact Modulation Calorimetry

Non-contact modulation calorimetry is a derivative of modulation calorimetry which features electromagnetic levitation (EML) and remote diagnostic tools. Usually small samples in the shape of sphere are levitated in an electromagnetic levitator in pure vacuum or a gas cooling atmosphere (Figure 1.17). Heating is provided with either radio frequency (RF) heating or laser beam. Thermophysical properties of the material are studied by analyzing the temperature response and dimensional change of the specimen recorded via remote optical pyrometer and high speed cameras. This
technique is suitable for measuring various thermophysical properties of high temperature metallic melts at both solid and liquid phase.

Figure 1.17. Skematic of an electromagnetic levitator with laser heating and gas cooling. The inset shows the configuration of RF-coil setting [4].

1.4.1 Advantages for Studying High Temperature Metallic Melts

The development of non-contact modulation calorimetry was spurred by the need of accurate thermophysical properties of high temperature metallic liquids in glass-forming alloys and quasicrystal research. However, the advantages brought by this technique should not be limited in this specific area, but rather applicable to a variety of conducting materials.

The greatest advantage of non-contact modulation calorimetry is that the test sample can be totally isolated and virtually in no contact with any external materials, which is however not feasible in all of the methods discussed above for $c_p$ and $k$ measurements. The benefits from this feature are twofold. Firstly, of course, there is no chemical contamination from the environment. This is extremely valuable for our
research given that potential quasicrytal-forming alloys are highly reactive at elevated temperatures. Secondly, using levitation technique reduces heterogeneous nucleation sites and thus deeper undercooling is available. This greatly facilitates the study of solidification kinetics of quasicrystals as the degree of icosahedral ordering in the undercooled liquids change with the degree of undercooling. Lastly, EML-MC excels in its versatility. Based on the same hardware platform, various different thermophysical properties can be measured, such as density, thermal expansion, surface tension, viscosity, specific heat, electrical resistivity, total hemispherical emissivity and thermal transport properties [101, 30, 100, 92, 34].

1.4.2 Background

The initial inspiration of this method came from the study of thermophysical properties of individual micron size particles. Monazam, et al., in 1989 measured $c_p$ and absorptivity of small particles with 0.05 ~ 0.2 mm in diameter [66]. Levitation was realized via electromagnetic balance. Modulated pulses at 100Hz with 3-ms period generated by a well-characterized CO$_2$ laser was casted onto the specimen levitated in a vacuum chamber to provide heating. The temperature fluctuation of the particle was recorded with high-speed pyrometer. The authors measured $c_p$ and absorptivity at temperature ranging from 800K to 1200K and the results were in fairly good agreement with published data.

Later, since 1991, Wunderlich, Fecht and other scientists published a series of papers to formally introduced EML based non-contact modulation calorimetry (EML-MC)[31]. The proposed method can be used to measure $c_p$ of stable and undercooled metals and alloys at high temperatures. For validation, preliminary experiments were conducted on solid niobium (Nb) in a prototype equipment TEMPUS [99, 103, 32]. The results under terrestrial environment were satisfactory but not without challenges, for example, intense heat and mass transfer through convection and surface
shape fluctuation due to strong positioning force required to counteract gravity prevent investigations on stable undercooled metallic liquids. Hence, EML-MC was further taken to the space on two shuttle missions: IML-2 and MSL-1 spacetlab, Wunderlich, et al., applied this method to Zr-Ni and Co-Fe binary eutectics with modified equipment. Due to decreased requirement on positioning force and thus smaller stirring effect, accurate measurements of $c_p$, enthalpy of fusion and some thermal transport properties of tested materials were obtained. Nevertheless, Wunderlich has pointed out that computational modeling of the combined heat and mass transfer effect within the sample is still needed for accurate determination of $k$ [98, 97, 102].

Recently, while researches gradually die down in Europe and the United States due to the discontinuation of space shuttle program, non-contact modulation calorimetry starts to attract more attention from Japan. Yasuda, et al., [105] have found that liquid specimen in EML behaves like a hard sphere in static magnetic field. Specifically, oscillation and convection of the droplet were significantly suppressed due to the effect of Lorentz force. Based on this study, Fukuyama, et al., designed another type of EML-MC in which the sample was levitated by static magnetic field and the heating was provided by laser. With a view to accurately measure $k$ value of high temperature molten materials, this method was proof tested on solid platinum samples and effect of the static magnetic field on the measured properties were analyzed [34, 5, 87]. Further practical applications of this method were mainly carried out on molten silicon droplets [54, 53].

### 1.4.3 Computational Study

There are only a few computational studies on EML-MC till now. Etay, et al., comprehensively evaluated the theoretical model and applications of EML-MC on thermophysical measurements of high temperature materials. They started out using ANSYS Fluent to examine assumptions used in the heat flow model proposed by
Wunderlich, et al. [102], which serves as the theoretical basis of current EML-MC. Their results show that under ideal conditions, i.e. solid samples under pure heater heating and relatively homogeneous internal temperature distribution, the model predicts the temperature response of the sample very precisely and EML-MC based $c_p$ measurement is very accurate under such condition [76]. Later, they extended their research of EML-MC on thermal measurements of liquids. Computational results show that convection due to EML stirring leads to an overestimation of $k$ but no negative impact on $c_p$. However, they were not able to quantify the contribution of convection and the simulations are limited to specimens with relatively homogeneous internal temperature distribution [75]. Besides $c_p$ and $k$ measurements, they also examined EML-MC for surface tension and viscosity measurement. Using lab developed codes, they were able to reproduce the shape of the levitated sample very close to what has been observed in the experiment. The EML process for surface tension and viscosity measurements are simulated. The computational results show a very good agreement in the determined surface tension between simulation and experiment. However, there's a comparatively large discrepancy in the viscosity. The difference is believed to be a result of the fact that the helicity of the coil and possible turbulent flow in the processed sample is not taken into account [28].

In a more recent effort, they revised conventional EML-MC by introducing pseudo-white noise modulation and system identification technique commonly seen in electronics and communication engineering [77]. This new technique is believed to be able to provide accurate thermophysical properties when internal temperature variation is large. Based on their previous research, they concluded that the sample can be treated as a black box in thermal analysis and the temperature response of the sample has a pure linear relationship with the power modulation. Hence, by applying a designed power modulation in the form of white-noise, the transfer function of such relationship can be identified. Since, the same transfer function can also be
solved analytically with Laplace transform based on the heat flow model proposed by Wunderlich, et al., equating both would gives $c_p$ and internal heat transfer coefficient of the test substance. Despite the novelty of this method, it is still bounded by some advantages inherited from the theoretical heat transfer model, i.e. limited applications only for solid samples and simple heating.

1.5 Research Objective

This research focuses on using numerical simulation to evaluate and extend the application of EML-MC for $c_p$ and $k$ measurements in a quantitative way. Firstly, EML based $c_p$ measurement for solid Niobium is simulated. The operational principles of EML-MC based on the theoretical heat flow model are evaluated in both ideal and unideal conditions. And a new $c_p$ testing configuration based on existing EML hardware is proposed for extend measurement range. Secondly, based on thermal measurements of a Zirconium based glass-forming alloy, a first ever feasibility study of using EML-MC to measure thermal conductivity of high temperature liquid materials is presented. Hypothetical experiments are conducted using numerical simulations with COMSOL to quantify the accuracy of such measurements under different convective interference levels. The effective application range is determined. Lastly, the possibility of combining experiment and numerical simulation to accurately determine thermophysical properties is discussed.
CHAPTER 2
ANALYTICS AND PRINCIPLES OF EML-MC

In this chapter, the experimental set-up, analytical treatment and operational principles of EML-MC will be introduced.

2.1 Experimental Set-up

Core experimental set-up of EML-MC includes an EML levitator and peripheral remote diagnostic tools, such as pyrometers and high speed cameras. Typically, spherical samples made of conductive materials are levitated and simultaneously heated by the alternating EM fields created by the radio-frequency (RF) coils (Figure 2.1 (a)). For instance, figure2.1 (b) demonstrates the layout of RF coils in MSL-1 TEM-PUS. Usually, two groups of coils can be distinguished, positioning coils and heating coils. The former is closer to the midplane and creates a quadruple E.M. field due to internal opposite running alternating currents. The resulting positioning force field fixes the sample in the center of the coil. And since this equilibrium position has effectively the lowest strength in the quadruple field, minimal heating is provided by the positioning coils. The heating input is mainly provided by the heating coils, with which a dipole E.M. field is created and induces electrical currents localized in the surface layer in the sample and causes Joule heating.

Thermalphysical properties of the test material, such as $c_p$ and $k$ can be evaluated by analyzing the induced thermal and dimensional response from modulating the heating or positioning current.
2.2 Analytical Solution

Analytical solution of EML-MC problem was initially developed by Fetch and Johnson in 1991 [31]. Later, a more comprehensive and complete account was published in 2005 by Wunderlich and Fecht [102].

2.2.1 Heat Flow Model

The mathematical model considers a rigid spherical sample levitated in an EML levitator. According to the classic electromagnetic theory, the primary, heater-dominated inductive heating profile adopts an axisymmetric shape as shown in Figure 2.2 (a) with maximum at equator and decrease exponentially towards the center. Quantitatively, the way that the induction heating penetrates into the sample can be characterized by skin depth ($\delta$), which is a quantity that describes the AC density distribution within a conductor:

$$\delta = \sqrt{\frac{2}{\mu \omega \sigma_e}}$$  \hspace{1cm} (2.1)

where, $\omega$ is the angular frequency of the current while $\mu$ and $\sigma_e$ is the absolute magnetic permeability and the electrical conductivity of the sample respectively.
Next, by approximating the continuous distribution of volumetric heating, a heat flow model which consists of a directly heated volume and a conductively heated volume (Figure 2.2 (b)) can be developed. The former (denoted with H) will have a volume fraction $g_H$ and surface area fraction $s_H$, where $0 < g_H, s_H < 1$. While for the later (denoted with S), the volume and surface fractions are $1 - g_H$ and $1 - s_H$, respectively. The two volumes are connected with internal heat transfer coefficient $k_c$, which characterize the amount of heat transferred between the two parts per unit time and temperature difference. $k_c$ is expected to be a function of the thermal conductivity of the test material itself and also the heating distribution within the sphere with the following empirical form:

$$k_c = c_1 R k$$  \hspace{1cm} (2.2)
where, $c_1$ is a constant determined by the heating distribution and the actual internal flow. An explicit expression of $k_c$ would require analytical solution of the internal heat flow. For solids, an approximated expression of $k_c$ are given by Wunderlich, et al.,[97]

$$k_c = 4\pi (R - \gamma \delta) k$$

(2.3)

where $R$ is the radius of the sphere and $\gamma$ is a geometric factor that takes account of the geometrical dependence of the heating distribution. In the case of liquid samples, convection can also contribute to $k_c$ and analytical expression for $k_c$ is hard to gain.

As to the heat loss of the sample, a relatively simple scenario is considered which assumes that the environment was vacuum and radiation was the only viable transfer mechanism. The radiative boundary condition of the sample can be linearized with a external heat transfer coefficient $k_r$, defined by

$$P_{rad} = A\sigma \varepsilon (T^4 - T_{env}^4) = P_{rad_0} + k_r (T - T_0)$$

(2.4)

so that

$$P_{rad_0} = A\sigma \varepsilon (T_0^4 - T_{env}^4)$$

(2.5a)

$$k_r = A\sigma \varepsilon (T^3 + T^2 T_0 + TT_0^2 + T_0^3)$$

(2.5b)

where, $T_{env}$ is the environmental temperature, $A$ is the total surface area, $\sigma = 5.67 \times 10^{-8} \, W/m^2K^4$ is the Stefan-Boltzmann constant, $\varepsilon$ is the total hemispherical emissivity, $T$ represents the surface temperature under modulation. When the temperature modulation is small enough so that $T \approx T_0$,

$$k_r = 4A\sigma \varepsilon T_0^3$$

(2.6)

At last, before any further discussions, an important parameter should be introduced: the Biot number (Bi). For an object subject to a thermal gradient on the
surface, $Bi$ can be defined as the external heat transfer coefficient divided by internal heat transfer coefficient,

$$Bi = \frac{h l_C}{k} \quad (2.7)$$

After Wunderlich [102], we take $h = 4\sigma \varepsilon T^3$ as the heat transfer coefficient on the surface. $l_C$ is characteristic length, which is the radius of the sample. When $Bi$ is small, the temperature profile within the object will be uniform when a thermal gradient is applied to the surface. For the materials studied in this research, such condition is satisfied for a wide range of temperature. Consequently, the directly heated and conductively heated volume can be treated as two isothermal domains with temperatures as measured on the poles ($T_H$) and equator ($T_S$). The initial equilibrium temperature of each domain before modulation can be approximated to be the same, $T_{H_0} = T_{S_0} = T_0$.

### 2.2.2 Temperature Response

The governing equations that describe the temperature response of coupled heat flow model can be established by assuming constant material properties:

$$g_H m c_p T_H(t) = P(t) - k_c [T_H(t) - T_S(t)] - s_H A \sigma \varepsilon (T_H^4(t) - T_{env}^4) \quad (2.8a)$$

$$(1 - g_H) m c_p T_S(t) = k_c [T_H(t) - T_S(t)] - (1 - s_H) A \sigma \varepsilon (T_S^4(t) - T_{env}^4) \quad (2.8b)$$

$P(t)$ is the total heating power which consists of a constant part $P_0$ and a oscillating part $P_{mod}(t)$.

$$P(t) = P_0 + P_{mod}(t) \quad (2.9)$$

where, $P_0$ contains heating effects from both heating coils $P_{H_0}$ and positioning coils $P_{P_0}$ and maintains equilibrium temperature $T_0$ before modulation. While $P_{mod}(t)$ is the modulated power input usually from the heating current modulation,

$$P_{mod}(t) = P_{av} + P_{\omega sin}(\omega t + \Phi_0) + P_{2\omega sin}(2\omega t + \Phi_0) \quad (2.10)$$
where, $P_{av}$ is the increase in the average heating input comparing to $P_{H0}$, $P_{\omega}$ and $P_{2\omega}$ correspond to the amplitude of power modulation at angular frequency $\omega$ and $2\omega$ respectively. In practice, current modulation was usually chosen with $P_{\omega} \gg P_{2\omega}$ so that $P_{2\omega}$ can be ignored.

Subtracting $P_0$ from the equation 2.8 (a) and substituting in the linearized boundary condition, the change in $T_H$ and $T_S$ subjecting to the modulation $P_{mod}(t)$ follows,

$$\Delta \dot{T}_H(t) = \frac{P_{mod}(t)}{g_Hmc_p} - k_{ch}[\Delta T_H(t) - \Delta T_S(t)] - k_{rh}\Delta T_H(t)$$

(2.11a)

$$\Delta \dot{T}_S(t) = k_{cs}[T_H(t) - T_S(t)] - k_{rs}\Delta T_S(t)$$

(2.11b)

where, $k_{rh}, k_{rs}$ and $k_{ch}, k_{cs}$ are radiative heat transfer coefficients and conductive heat transfer coefficients corresponding to each of the domains in the heat flow model.

$$k_{rh} = \frac{s_H}{g_Hmc_p}k_r$$

$$k_{rs} = \frac{1 - s_H}{(1 - g_H)mc_p}k_r$$

(2.12)

$$k_{ch} = \frac{1}{g_Hmc_p}k_c$$

$$k_{cs} = \frac{1}{(1 - g_H)mc_p}k_c$$

(2.13)

This set of first order differential equations (ODEs) can be treated as a simple matrix ODE and solved by diagonalizing the coefficient matrix. If Bi number is smaller than, according to Wunderlich, et al., 0.01, eigenvalues of the coefficient matrix $\lambda_1$ and $\lambda_2$ can be approximated,

$$\lambda_1 \approx -\frac{k_r}{mc_p}$$

(2.14a)

$$\lambda_2 \approx -\frac{k_c}{mc_p g_H (1 - g_H)}$$

(2.14b)

Allowing definitions of external and internal relaxation time $\tau_1, \tau_2$ and also the evaluation of Biot number,
\[ \tau_1 = -\frac{1}{\lambda_1} \quad (2.15a) \]
\[ \tau_2 = -\frac{1}{\lambda_2} \quad (2.15b) \]
\[ B\dot{t} = \frac{\lambda_1}{\lambda_2} = \frac{\tau_2}{\tau_1} \quad (2.15c) \]

Since \( k_c \gg k_r \), \( \tau_1 \gg \tau_2 \) and the transient response of the system is dominated by \( \tau_1 \). For the heating modulation in equation 2.10, the temperature changes in the inductively and conductively heated domain are obtained,

\[ \Delta T_H(t) = \Delta T_{Hav}[1-e^{\lambda_1 t}] + T_{HTr} \sin(\Phi_0 + \phi_{Tr}) e^{\lambda_1 t} + \Delta T_o f_H \sin(\omega t + \Phi_0 + \phi_H) \quad (2.16a) \]
\[ \Delta T_S(t) = \Delta T_{Sav}[1-e^{\lambda_1 t}] + T_{STr} \sin(\Phi_0 + \phi_{Tr}) e^{\lambda_1 t} + \Delta T_o f_S \sin(\omega t + \Phi_0 + \phi_S) \quad (2.16b) \]

The first term on the right hand side is the temperature response due to \( P_{av} \) with,

\[ \Delta T_{Hav} = \Delta T_{Sav} = \frac{\Delta P_{av} \tau_1}{mc_p} \quad (2.17) \]

The second term is a transient response due to \( P_{mod}(t) \) with phase lag \( \phi_{Tr} \) given by \( \cos\phi_{Tr} = \lambda_1(\lambda_2^2 + \omega^2)^{-1/2} \). For simplicity of the processing of the temperature signal, this term is usually suppressed by choosing \( \Phi_0 = -\phi_{Tr} \) and this is why \( \Phi_0 \) was initially introduced. A typical temperature signal measured on the north pole of the sample is shown in figure 2.3.

The gradual increase in average temperature of the signal corresponds to the first term of \( \Delta T_S(t) \) while modulation reflects the third term of \( \Delta T_S(t) \) which is the stationary modulation response due to \( P_{mod}(t) \). The amplitude of the modulation is given by \( \Delta T_o f_S \), where

\[ T_o = \frac{P_o}{mc_p \omega} \quad (2.18) \]
And,

$$f_S(\omega, \lambda_1, \lambda_2) = \frac{k_{cs}}{g_H}[\omega^2 + \lambda_1^2][\omega^2 + \lambda_2^2]^{-1/2}$$

$$\cos \phi_S = (\lambda_1 \lambda_2 - \omega^2)[(\omega^2 + \lambda_1^2)(\omega^2 + \lambda_2^2)]^{-1/2}$$

Similarly for the directly heated volume,

$$f_H(\omega, \lambda_1, \lambda_2) = \frac{\omega}{g_H}[\omega^2 + \lambda_2^2]^{-1/2}[(\omega^2 + \lambda_1^2)(\omega^2 + \lambda_2^2)]^{-1/2}$$

$$\cos \phi_H = \frac{-[c_4(\omega^2 - \lambda_1 \lambda_2) + \omega^2(\lambda_1 + \lambda_2)]}{[(\omega^2 + \lambda_1^2)(\omega^2 + \lambda_2^2)]^{-1/2}}$$

Where, $$c_4 = k_{cs} + k_{rs}$$.

### 2.3 Principles of EML-MC

#### 2.3.1 $c_p$ Measurement

Theoretically, either equation 2.17 or 2.18 can be used to calculate $c_p$. Equation 2.17 provides the simplest way of measuring $c_p$ which is to apply just a small step-change in the heating current, without modulation, to induce a small enough
temperature variation that the linearization of the thermal boundary is valid. Then $\Delta T_S(t)$ can be reduced to only the first term in equation 2.16 resulting,

$$c_p = \frac{\Delta P_{av} \tau_1}{\Delta T_{Sav} m}$$

(2.23)

$\tau_1$ can be obtained by fitting a first-order exponential decay curve to the smoothed temperature signal measured at the polar position (Figure 2.4). When EML-MC is operating at power modulation mode which generates a time temperature curve similar to figure 2.3, the temperature response of $\Delta T_S(t)$ due to $P_{av}$ can still be separated from the lumped temperature signal by subtracting the modulation part. Then, the same procedure can be applied to obtain $\tau_1$ and thus $c_p$.

Considering that the evaluation of $\tau_1$ requires certain amount of data processing from the noise-masked time temperature profile, equation 2.18 is more preferred in EML-MC experiments. With $P_\omega$, $m$ and $\omega$ known from the experiment, $c_p$ can be calculated with,

$$c_p = \frac{P_\omega}{m \omega T_\omega f_S(f_H)}$$

(2.24)

**Figure 2.4.** A time-temperature profile of $Zr_{64}Ni_{36}$ sample when heating is turned down and temperature decays to equilibrium [98].
$f_S$ and $f_H$ is plotted in figure 2.5 for different Bi numbers. Since obviously, they cannot be obtained from the experiment, the question now boils down to the identification of the modulation frequency range where $f_H$ and $f_S \approx 1$ and $c_p$ can be measured without considering the correction function. When $Bi \ll 0.01$, the analytical expression for

\begin{align}
    f_S(\omega, \lambda_1, \lambda_2) &= \left[ 1 + \frac{\omega^2}{\lambda_2^2} + \frac{\lambda_1^2}{\omega^2} \right]^{-1/2} \\
    f_H(\omega, \lambda_1, \lambda_2) &= \left[ 1 + \frac{\omega^2}{\lambda_2^2 g_H^2} \right] \left[ 1 + \frac{\omega^2}{\lambda_1^2} + \frac{\lambda_1^2}{\omega^2} \right]^{-1/2}
\end{align}

Differentiating equation 2.25a with respect to $\omega$, a modulation frequency $\omega_{\text{max}}$ can be found that a finite frequency window nearby satisfies $|1 - f_S(\omega, \lambda_1, \lambda_2)| \leq 10^{-2}$.

$$\omega_{\text{max}} = \sqrt{\lambda_1 \lambda_2}$$

Conventionally, this condition is called isothermal modulation and the $\omega$ range is referred to as isothermal modulation frequency. And, since $\omega_{\text{max}}$ gives $\cos(\phi_S) = 0$, 

\textbf{Figure 2.5.} Correction functions $f_S$ (full lines) and $f_H$ (dashed lines) for different Bi numbers [102].
which implies \( \phi_S = 90^\circ \), the best way of identifying isothermal modulation frequency is to measure \( \phi_S \).

In practice, a looser constraint on Bi is acceptable. According to Wunderlich, \textit{et al.}, \(|1 - f_S(\omega_{\text{max}}, \lambda_1, \lambda_2)| \leq 3 \times 10^{-2}\) is available for Bi up to 0.05. At this range, effect of \( f_S \) or \( f_H\) needs to be factored in to correct the amplitude of measured temperature modulation. Due to explicit dependence of \( f_S \) on \( g_H \), which is hard to be determined experimentally, it is suggested that \( c_p \) should be measured based on the equatorial temperature \( T_H(t) \). However to identify a frequency that gives \( f_H \approx 1 \) remains to be a question. [102].

2.3.2 k Measurement

With \( \lambda_1 \) obtained from applying step change heating power or separating temperature response due to \( P_{av} \) from figure 2.3, \( \lambda_2 \) and thus internal thermal transfer coefficient \( k_c \) can be calculated from equation 2.20 by measuring \( \phi_S \). Now that \( k_c \) is known, \( k \) can be evaluated based on the analytical solution of \( k_c \), which unfortunately is only available as different approximation forms.

For solids, Fecht and Johnson proposed an expression for \( k_c \) based on similar heat transfer problems [31, 16],

\[
k_c = \frac{4}{3} \pi^3 R k
\]  

Measurement with this expression proves to be acceptable with a systematic error up to 10\% [97]. However, further improvement with this method is impossible because derivation of this from is based on the assumption of spherical symmetric heating, which is not true for EML processing. Thus, a detailed modeling work is required to determine \( k \) with higher accuracy, especially when the sample is liquid and the contribution of convection in the relaxation of internal thermal gradient is significant.
2.3.3 Verification of Isothermal Modulation

As one may have noticed from foregoing deduction, isothermal modulation condition ($Bi \ll 0.01$) is the key to the accurate measurements of $c_p$ and $k$ with EML-MC. In order to verify this condition experimentally, Wunderlich, et al., have developed several characteristic behaviors of the sample in EML-MC based on the heat flow model: (i) by applying a step change heating power, the temperature measured at the poles and equator should follow a pure exponential decay curve with the same average temperature increase; (ii) by modulating the heating power at isothermal modulation frequency $\omega_{max}$, the amplitude of the stationary temperature modulation at the poles and equator should be the same to 2% and $\phi_S(\omega_{max}) = -\pi/2$ according to equation 2.20; and (iii) $Bi = \frac{Bi}{\alpha} \leq 0.01$.

2.3.4 Modulation Modes

The total heat input from RF coils consists of heating effect from the heater and the positioner,

$$P(t) = G_H I_H^2(t) + G_P I_P^2$$  \hspace{1cm} (2.28)

where, $G_H$ and $G_P$ are the coupling coefficients between the heater/positioner and the sample. Detailed procedures on how to obtained these coefficients for different EML coils can be found in [102].

Usually, the current modulation is applied to the heater. And, there are two modulation modes available in EML-MC: amplitude modulation and power modulation.

In the amplitude modulation mode, the heater current is modulated as $I_H(t) = [I_{H_0} + I_\omega(\omega t + \Phi_0)]^2$. And the resulting power modulation is,

$$P(t) = P_H(t) + P_{P_0} = P_{H_0} + P_{P_0} + \Delta P_{av} + P_\omega sin(\omega t + \Phi_0) + P_{2\omega sin}(2\omega t + \Phi_0)$$  \hspace{1cm} (2.29)

where,
\[ P_{H_0} = G_{H} I_{H_0}^2 \]  \hspace{1cm} (2.30a)

\[ P_I = G_{P} I_{P_0}^2 \]  \hspace{1cm} (2.30b)

\[ P_\omega = G_{H} 2I_{H_0} I_\omega \]  \hspace{1cm} (2.30c)

\[ \Delta P_{av} = P_{2\omega} = \frac{1}{2} G_{H} I_\omega^2 \]  \hspace{1cm} (2.30d)

At this mode, the induced temperature response is similar to Figure 2.3. Since \( c_p \) measurement requires accurate determination of \( T_\omega \) and \( T_{av} \) which are only available after the establishment of stationary temperature modulation, a waiting time up to \( t > 3\tau_1 \) is . This issue usually wouldn’t affect the design of experiments. However, when the investigated material is undercooled metallic melts as in Wunderlich’s research, this prerequisite can be an obstacle because crystallization can initiate before the end of this period [102].

Power modulation however is free from such issue. In this mode, the current signal is modulated in terms of the square root of a sinusoidal wave,

\[ I_H(t) = \left[ I_{H_0} + I_\omega (\omega t + \Phi_0) \right]^{1/2} \]  \hspace{1cm} (2.31)

So that there is only \( P_{H_0} \) and \( P_\omega \) term left in the modulated heating power. By operating in this mode along with a proper choice of \( \Phi_0 \), steady modulation can be achieved much faster than in amplitude modulation and quick measurements of \( c_p \) and other thermophysical properties are possible.
CHAPTER 3
MODELING OF EML-MC

This chapter presents the modeling work of EML-MC based on a commercial finite element solver: COMSOL, which is a multi-physics simulation software suitable for computational tasks involving coupled phenomena. In this chapter, firstly, the underlying physics of the EML process and its coupling scheme is introduced and analyzed. With proper simplification, the complexity of this problem is reduced in accordance to the research objective. Secondly, modeling of different physics of the EML process is presented and validated against previous computational work. Lastly, the meshing scheme for this particular problem is discussed. And a convergence analysis is conducted to determine the best mesh size for the following computational study.

3.1 Problem Simplification

The EML process is an inherently complex multi-physics problem. To properly model this problem, four physics need to be considered: electromagnetics, fluid dynamics, heat transfer and mechanical dynamics of the sample. They are closely coupled together as shown in the following diagram (Figure 3.1). A direct numerical simulation of this problem is not impossible but laborious and computational costly. Thus, proper approximation should be used.

In order to simplify the problem, as in the theoretical model, firstly we will assume that the sample maintains its position and shape without any tilting and periodic movement throughout the experiment. In reality, due to the helicity of the EML coil
Figure 3.1. Complete coupling scheme of underlying physics in EML-MC [28]. $\delta_{el}(T)$ is the temperature dependent electrical resistivity. Thermo-driven flow includes Marangoni flow and natural convection from the temperature dependence of surface tension and density respectively.
and residual accelerations of the international space station (ISS), the sample can be distorted and swung out of the center of coil [28]. Nevertheless, considering the amplitude of these movements is small and the potential benefit-cost ratio of taking account of the dynamics of the sample is low, this assumption will be adopted.

Secondly, in EML-MC, the temperature change in modulation ($T_{av}$ and $T_w$) is normally much smaller than the equilibrium temperature. So that changes in thermophysical properties of the test material can be safely neglected. As a result, EM effects can be calculated independent of thermophysical properties, such as electrical resistivity ($\delta_{el}(T)$). Furthermore, previous simulations by Hyers, et al., [43] have shown the thermally-driven flows, such as Marangoni flow and natural convection are orders of magnitude weaker than E.M. driven flow. Hence, these phenomena can also be neglected.

The last assumption addresses the coupling of electromagnetics and fluid dynamics. Table 3.1 lists typical timescales in EML process for a 7 mm diameter nickel sample with corresponding symbols and values in table 3.2 [42]. Obviously, the time scale for the magnetic field to reach equilibrium is much larger than charge relaxation time and electromagnetic wave transit time, that is, the EM effect of the system is dominated by the flow of induced current. Furthermore, since the magnetic Reynolds number [65], which dictates the influence of fluid flow on current flow,

$$\text{Re}_m = \frac{\tau_m}{\tau_{conv}} = \mu_0 \delta_{el} U_0 l_0$$ (3.1)

is much smaller than unit, the fluid flow does not significantly perturb the magnetic field. Therefore, the calculation of fluid flow could be decoupled with the the E.M. induced current. In summary, the EM effects can be calculated without considering the internal flow.
Table 3.1. Characteristic timescales important EML process [42]. Symbols and typical values are given below.

<table>
<thead>
<tr>
<th>Characteristic Time</th>
<th>Definition</th>
<th>Value (typical)</th>
</tr>
</thead>
<tbody>
<tr>
<td>electromagnetic wave transit time</td>
<td>$\tau_{ew} = \frac{l_0}{c}$</td>
<td>$1.17 \times 10^{-11}$ s</td>
</tr>
<tr>
<td>charge relaxation time</td>
<td>$\tau_c = \frac{\varepsilon_0}{\delta_{el}}$</td>
<td>$7.38 \times 10^{-18}$ s</td>
</tr>
<tr>
<td>magnetic diffusion time</td>
<td>$\tau_m = \mu_0 \delta_{el} l_0^2$</td>
<td>$1.85 \times 10^{-5}$ s</td>
</tr>
<tr>
<td>material transit time</td>
<td>$\tau_{conv} = \frac{l_0}{U_0}$</td>
<td>$1.75 \times 10^{-2}$ s</td>
</tr>
</tbody>
</table>

Table 3.2. Symbols and typical values [42]

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l_0$</td>
<td>Reference length</td>
<td>$3.5 \times 10^{-3}$ m (typical)</td>
</tr>
<tr>
<td>$c$</td>
<td>Speed of light</td>
<td>$2.9979 \times 10^8$ m/s</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>Electrical permittivity of metals</td>
<td>$8.845 \times 10^{-12}$ F/m</td>
</tr>
<tr>
<td>$\delta_{el}$</td>
<td>Electrical conductivity</td>
<td>$1.2 \times 10^6$ (\Omega m)$^{-1}$</td>
</tr>
<tr>
<td>$\mu_0$</td>
<td>Magnetic permeability of metals</td>
<td>$4\pi \times 10^{-7}$ H/m</td>
</tr>
<tr>
<td>$U_0$</td>
<td>Reference velocity</td>
<td>$5$ cm/s (typical for microgravity EML)</td>
</tr>
</tbody>
</table>

With all these simplifications, the EML process can now be described as an semi-coupled heat and mass transport problem driven by inductive EM fields (Figure 3.2).

3.2 Modeling of EM induced forces and heating

The E.M. part of the problem, E.M. induced stirring force and power input into the sample, is tackled first due to its sole dependence on the current of the levitation coils and previously postulated constant materials properties. A software kit named “mags” originally written by Hyers is used to calculate EM induced forces and heating[42]. The underlying principles of the software is developed by the research group of Prof. Julian Szekely [26, 109, 107, 108]. Specifically, this electromagnetic calculation method is based a two-dimensional axisymmetric model using the volume integral method. The levitated sample is discretized into small rectangular elements.
(Figure 3.3) and their interaction as well as the effect of externally imposed E.M. effect by the levitation coil is calculated. This method can be used to calculate the E.M. stirring force and absorbed power by the sample for any arbitrary axisymmetric coil, on any arbitrary axisymmetric sample. However, due to the assumption of axisymmetry, this method is not able to evaluate radial restoring force when the sample is off-center. Despite these limitations, the method and named “mags” align perfect with the computational requirement and research objective of current study.

Figure 3.4 (a) and (b) shows the induction heating distribution from unit heating/positioning current in TEMPUS coil. Axis Y corresponds to the direction defined by the rotating axis and should align with the symmetric axis of the levitation coil, while axis X is the radial direction perpendicular to Y direction. Comparing the legends between both figures, it is obvious that unit current in heater produces much more heating than the same current in positioner. Hence, when the magnitude of $I_H$ is larger or comparable to $I_P$, the total heating distribution will be dominated by the heater and displace similar profile as in the Figure 3.4 (a).
Figure 3.3. A typical $20 \times 20$ grid for electromagnetic calculation in mags.

Figure 3.4. EM heating profile due to unit heating and positioning current calculated with “mags” for 1840K solid niobium.
The total heating for the model can be written as a superimposition of heater heating and positioner heating with each being proportional to the square of corresponding current strength,

\[ P(t) = I_H^2 \cdot HHS + I_P^2 \cdot PHS \]  \hspace{1cm} (3.2)

where, HHS, PHS are heat sources from unit heater and positioner current. Comparing to equation 2.28, effectively, \( HHS = G_H \) and \( PHS = G_P \). The current modulation, and in fact any arbitrary power modulation can be replicated by plugging in the functional form of current modulation into \( I_H \), or \( I_P \).

The body force imposed by the levitation coils is effectively the Lorentz force exerted by induced external electromagnetic fields on skin current. “mags” calculates the X and Y components of the body force from the heating and positioning coil (Figure 3.5). The total stirring force of the levitation coils is again the superimposition of force fields from the heater and the positioner.

![Figure 3.5](image_url)

(Figure 3.5. Plot of radial (HFX, PFX) and axial (HFY, PFY) component of the Lorentz force exerted by the heating and positioning coils with unit current.)
3.3 Modeling of Internal Fluid Dynamics and Heat Transfer

The internal flow of the sample is governed by the continuity equation and the Navier-Stokes equation,

\[
\nabla \cdot \mathbf{u} = 0
\]

\[
\rho \frac{\partial \mathbf{u}}{\partial t} + \rho (\mathbf{u} \cdot \nabla) \mathbf{u} = \mu \nabla^2 \mathbf{u} - \nabla P + \mathbf{F}_{EM}
\]

where, density \( \rho \) is a constant which is not affected by either pressure change or temperature change. \( \mathbf{F}_{EM} \) is the E.M. stirring force from the RF coils. \( \mathbf{u} \) represents the internal flow and \( \mu \) the constant viscosity.

The boundary condition for this flow can be described as a free surface, that is no shear stress on the surface and also the flow is pure tangential on the surface,

\[
\left. \frac{\partial u_\theta}{\partial r} \right|_{r=R} = 0
\]

\[
\left. \mathbf{u} \cdot \hat{\mathbf{r}} \right|_{r=R} = 0
\]

The heat flow within the sample is governed by the energy equation,

\[
\rho c_p \frac{\partial T}{\partial t} + \rho c_p (\mathbf{u} \cdot \nabla T) = k \nabla^2 T + Q_{EM}
\]

where, \( T \) is the temperature field and \( Q_{EM} \) is the E.M. heating from the RF coils.

For simplicity, thermal boundary condition is treated as pure radiative with uniform environmental temperatures,

\[
-k \left. \frac{\partial T}{\partial r} \right|_{r=R} = q_{rad} = \varepsilon \sigma (T^4 - T_{env}^4)
\]

The environmental temperature is usually 100-150°C for the EML-MC experiments studied in this research.
The fluid dynamics and heat transfer phenomena are simulated with laminar fluid flow and heat transfer module in COMSOL, respectively. The former was chosen based on the fact that the glass-forming alloys we are interested are generally highly viscous even at very high temperatures.

3.4 Model Validation

Conventionally, in order to validate a numerical model, the best way is to directly compare simulation results to experiments. In our case, the E.M. stirring force and power calculation has already been validated by previous work [42]. However, it is impossible to validate the fluid dynamics and heat transfer calculations in our model. The difficulty comes from the inability of measuring flow velocity of levitated droplets in EML process. The sample is usually opaque and featureless which rules out Doppler velocimetry. Electromagnetic sensors, such as Vives probe, cannot provide meaningful data due to the extreme test condition i.e. high temperature, high sample reactivity and large E.M. field. Seeding the sample and using particle imaging velocimetry also falls short of our goal. Because the seed particle will be sweep into stagnation lines in the formed flow field[57]. Hence, in order to validate the utility of this model, simulation results obtained from this model are compared to similar computational studies performed by Hyers, et al., with FIDAP, which is another commercial finite element code for computational fluid dynamics [44].

Firstly, a stationary analysis which involves only the flow module was performed for an FeCrNi alloy. Table 3.3 lists thermophysical properties for this alloy at melting point from [44]. This reference also contains a supportive argument on our assumption of constant material properties under small temperature modulations.

Heater or positioner dominated stationary flow patterns were simulated with the COMSOL model (Figure 3.6). In comparison to the results of Hyers, et al., the flow patterns are the same. For the heater flow, two symmetric single recirculation
Table 3.3. Thermophysical properties of FeCrNi alloy [44]

<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>ρ</td>
<td>7,040 kg/m³</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>k</td>
<td>28.4 W/m-K</td>
</tr>
<tr>
<td>Specific heat capacity</td>
<td>cₚ</td>
<td>830 J/Kg-K</td>
</tr>
<tr>
<td>Viscosity</td>
<td>μ</td>
<td>5.59×10⁻³ Pa-sec</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>σₑ</td>
<td>6.63×10⁷(Ω·m⁻¹)</td>
</tr>
<tr>
<td>Total hem. emissivity</td>
<td>εₜ</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Loop form with inward flow at the equator, which is consistent with the location of maximum centripetal force as in Figure 3.5 (a). For the positioner flow, each of the symmetric heating zones (Figure 3.4 (b)) induces 2 recirculation loops in the top and bottom hemisphere of the sample. Corresponding to the positioner force field (Figure 3.5 (b)), fluid flow inward at ±45° latitude and outward at locations with minimum EM fields, which is the equator and poles. To compare quantitatively, the maximum flow velocity is 5.6 cm/sec and 2.3 cm/sec for the heater flow and positioner flow from current study while Hyers reported 5.5 cm/sec and 1.9 cm/sec. The larger values can be attributed to the finer mesh adopted in current model which better captures the flows very near surface where the velocity gradient is large.

Next, in order to test the model’s full functionality, isothermal holding of the FeCrNi alloy under heater dominated heating, is simulated. The computational result with the COMSOL model displayed the same heating distribution and flow pattern as in Hyers’ model. However, the average equilibrium temperature from current model is higher. This discrepancy can be attributed to the difference in the modeling of thermal boundary. In his study, the sample is levitated in a gas mixture. So there is an extra term in heat loss through conduction which resulted in a lower equilibrium temperature.
Figure 3.6. Simulation of heater dominated stationary flow ($I_H = 40A$ and $I_P = 150A$) and positioner dominated stationary flow ($I_H = 0$ and $I_P = 150A$).

Figure 3.7. Electromagnetic heating distribution (left) and temperature profile of FeCrNi alloy (right) under isothermal holding simulation ($I_H = 135A$ and $I_P = 150A$). The maximum temperature of the sample is 1543.7K and the minimum 1539.9K. Maximum surface temperature difference is 1.38K.
3.5 Meshing

The numerical model for the problem under consideration is rather simple, a sphere. Intuitively, it would be conveniently to mesh the model with the default triangular mesh. However, the underlying phycis requires something else. In EML, the internal fluid flow and heat transfer is powered by the EM effect from the levitation coils. The domain of EM effect is characterized by skin depth as shown in Figure 3.4 and 3.5. And the intensity of such effect decreases exponentially from surface to the center. So, in order to better accommodate the large thermal gradient and flow velocity near the surface, more grid points should be placed in the skin area.

Figure 3.8 shows the mapped mesh used in currently study. The whole domain is divided into two areas. The inner area is a half hexagon with edge equaling one fifth of the radius of the sphere. The size of the inner hexagon is somewhat arbitrary. The overall thermal response of the system is weakly dependent on the size of the inner hexagon because the corresponding E.M. field is weak and this core area is relatively quiescent compared to the surface. This region is created to prevent otherwise slender elements near the center of domain with large aspect ratio. In the outer region, the size of the elements in radial direction follows an arithmetic distribution with the largest element being 10 times thicker than the thinnest on the surface. The resulting mesh is similar to what has been used in the mags. Using this mesh can minimize the mismatch between the mesh used in mags and COMSOL and thus reduce interpolating error.

In current study, different coil settings and materials are studied. For simplicity and consistency consideration, a mesh convergence study is conducted based on the worst condition, meaning the largest thermal gradient and flow velocity near the surface of the sample, of all that is planned to be studied. And the determined mesh would be used for all simulations. The convergence analysis is conducted based on thermal measurements of a zirconium based alloy: $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ at 1033K
Figure 3.8. Meshing scheme for the 2D axisymmetric model in COMSOL.

The material’s properties are listed in table 3.4 which is obtained from either experimental data during MSL-1 Spacelab mission or estimation based on materials with similar compositions. Note the electrical conductivity is enlarged 4 times relative to the true value to manually create the worst condition and a viscosity value is given to this solid material to test the mesh’s utility for fluid flow calculation.

Table 3.4. Properties of Zr$_{65}$Al$_{17.5}$Cu$_{17.5}$Ni$_{10}$ at 1033K.

<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius</td>
<td>R</td>
<td>4.035mm</td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>$\rho$</td>
<td>6647.4 Kg/m$^3$</td>
<td></td>
</tr>
<tr>
<td>Electrical Conductivity</td>
<td>$\sigma_{el}$</td>
<td>$3.48 \times 10^5 (\Omega m)^{-1}$</td>
<td>[97]</td>
</tr>
<tr>
<td>hemispherical emissivity</td>
<td>$\varepsilon$</td>
<td>0.23</td>
<td>[101]</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>$k$</td>
<td>21W/mK</td>
<td>[97]</td>
</tr>
<tr>
<td>Specific heat capacity</td>
<td>$c_p$</td>
<td>366.5J/KgK</td>
<td>[101]</td>
</tr>
<tr>
<td>Viscosity</td>
<td>$\mu$</td>
<td>0.27</td>
<td>[13]</td>
</tr>
</tbody>
</table>

*The electrical conductivity is enlarged 4 times than the true value to manually create the worst condition.
The measurement on Zr alloy is conducted with TEMPUS coils as shown in Figure 2.1 (b). The heater and positioner current are 160.4A and 25A, respectively. Considering the manually increased electrical conductivity which results in a change in absorbed power by the sample, currents in the model is scaled to maintain the experimental temperature. The environment temperature is set at room temperature, 300K. Isothermal holding of the sample is simulated with different mesh density in both mags and COMSOL. The results of the analysis is listed in table 3.5. Figure 3.9 plots the dependence of the polar equilibrium temperature of the sample on mesh size.

**Table 3.5.** Mesh convergence analysis based on isothermal holding of ZrAlCuNi alloy

<table>
<thead>
<tr>
<th>Discritization in mags</th>
<th>Computational Time of mags(s)</th>
<th>Total Elements in COMSOL</th>
<th>Equilibrium $T_{pole}$</th>
<th>Computational Time of COMSOL(s)</th>
<th>$\Delta T$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20×20</td>
<td>10</td>
<td>432</td>
<td>1040.30471210221</td>
<td>6</td>
<td>5.04280638606</td>
</tr>
<tr>
<td>30×30</td>
<td>40</td>
<td>938</td>
<td>1035.26190571615</td>
<td>6</td>
<td>0.92576732342</td>
</tr>
<tr>
<td>40×40</td>
<td>160</td>
<td>1,662</td>
<td>1034.33613839273</td>
<td>8</td>
<td>0.57199010681</td>
</tr>
<tr>
<td>50×50</td>
<td>480</td>
<td>2,548</td>
<td>1033.76414828592</td>
<td>8</td>
<td>0.47512169540</td>
</tr>
<tr>
<td>60×60</td>
<td>1,500</td>
<td>3,638</td>
<td>1033.28902659052</td>
<td>9</td>
<td>0.15392752407</td>
</tr>
<tr>
<td>70×70</td>
<td>3,780</td>
<td>4,904</td>
<td>1033.13509906645</td>
<td>9</td>
<td>0.12276017611</td>
</tr>
<tr>
<td>80×80</td>
<td>9,120</td>
<td>6,424</td>
<td>1033.01233889034</td>
<td>12</td>
<td>0.08650439005</td>
</tr>
<tr>
<td>90×90</td>
<td>18,180</td>
<td>8,174</td>
<td>1032.92618886629</td>
<td>14</td>
<td>0.06843123038</td>
</tr>
<tr>
<td>100×100</td>
<td>36,000</td>
<td>10,024</td>
<td>1032.85775762991</td>
<td>17</td>
<td>0.03943128303</td>
</tr>
</tbody>
</table>

It is obvious that the polar temperature converges as the mesh size decreases. However, referring to the last column in the table, the convergence speed is not optimal. The gain from increasing element numbers is not proportional to the error being reduced. This convergence behavior is a direct result of the exponential distribution behavior in the E.M. intensity. In the region near the surface, very small elements is needed to handle the large thermal and fluid velocity gradient. Considering the computational resource available to this project, a desktop computer with a 2.67GHz Intel i7 cpu and 3 GB RAM, the $80 \times 80$ mesh is used for the following computational studies.
Figure 3.9. Mesh convergence analysis. Based on thermal measurement of liquid Zr$_{65}$Al$_{7.5}$Cu$_{17.5}$Ni$_{10}$ at 1033K during MSL-1 Spacelab mission [97]. The numbers on the abscissa correspond to discritization in mags from $10 \times 10$ to $110 \times 110$. 
CHAPTER 4
NUMERICAL STUDY OF SPECIFIC HEAT MEASUREMENTS WITH EML-MC

In this chapter, measurement of specific heat ($c_p$) of solid niobium (Nb) is modeled and the utility of the operational principles of EML-MC at low Bi number is confirmed. Then, by scaling the sample size, virtual experiments with high Bi numbers are studied for current EML apparatus. Lastly, simulation results at this Bi range are presented with utility of EML-MC theory at high Bi numbers discussed.

4.1 Experiment on Solid Nb

EML-MC, as a containerless processing technique, is suitable for the high temperature research of quasicrystals and glass-forming alloys. To prove its usefulness and also to justify its employment on the International Space Station (ISS), preliminary experiments are carried out on Solid Nb [99, 103, 32]. These experiments are performed in a prototype EML equipment named TEMPUS with coil setting shown in Figure 2.1 (b). To prevent overheating problems commonly seen in terrestrial EML processes due to large working current required for levitation, the 10 mm diameter solid sample is actually hanging in the center of RF coils with a thin wire. Given that the dimension of the supporting wire is small compared to the test object, its influence on overall thermal balance and thus the measurement are neglected. The heater current is modulated in amplitude mode to provide fluctuating power input to the sample. $c_p$ of solid niobium is measured at two temperatures, 1705K and 1840K. Table 4.1 summarizes the measurement results as well as some important parameters.
in the experiment. Note that the $\tau_1$’s in the table are obtained by fitting curve to the time temperature profile obtained through step change in heating current.

Table 4.1. $c_p$ measurement of solid Nb and important parameters in the experiment [103].

<table>
<thead>
<tr>
<th>$T_0$</th>
<th>Frequency ((s^{-1}))</th>
<th>$\tau_1$ ((s))</th>
<th>$\tau_2$ ((s))</th>
<th>$c_p$ ((J/kgK))</th>
<th>Literature Value ((\text{Ref. } [6]))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1705</td>
<td>0.08</td>
<td>14.7±0.2</td>
<td>0.12</td>
<td>330.4±6.5</td>
<td>333</td>
</tr>
<tr>
<td>1840</td>
<td>0.08</td>
<td>17.8±0.2</td>
<td>N/A</td>
<td>342.3±6.5</td>
<td>341.4</td>
</tr>
</tbody>
</table>

Figure 4.1 shows the time temperature profile for the Nb sample under power modulation mode at 1840K for two different frequencies.

![Figure 4.1](image)

**Figure 4.1.** Control voltage of the RF coils (upper trace) and corresponding time temperature profile (lower trace) of a 10mm diameter Nb sample subject to power modulation with frequency $f = 0.08s^{-1}$ (left) and $f = 0.4s^{-1}$ (right) [32].
4.2 Simulation of $c_p$ Measurement

The simulated measurement is the one at 1840K. Table 4.2 lists the corrected dimension and thermophysical properties of the test specimen. Since the sample is solid, fluid dynamics is out of the equation and the laminar flow module can be turned off.

**Table 4.2.** Corrected dimension of the sample and thermophysical properties of Nb at 1840K.

<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear Thermal Expansion</td>
<td>$\Delta L/L_0$</td>
<td>1.36%</td>
<td>[36]</td>
</tr>
<tr>
<td>Corrected Radius</td>
<td>$R$</td>
<td>5.068mm</td>
<td></td>
</tr>
<tr>
<td>Corrected Density</td>
<td>$\rho$</td>
<td>8229.6Kg/m$^3$</td>
<td>[36]</td>
</tr>
<tr>
<td>Electrical Conductivity</td>
<td>$\sigma_{el}$</td>
<td>$15.4 \times 10^5(\Omega m)^{-1}$</td>
<td>[95]</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>$k$</td>
<td>78.59W/mK</td>
<td>[91]</td>
</tr>
<tr>
<td>Specific heat capacity</td>
<td>$c_p$</td>
<td>341.4J/KgK</td>
<td>[6]</td>
</tr>
</tbody>
</table>

The heating and positioning current in the RF coils is not reported, they need to be determined from the time-temperature profile. Before doing this, coupling coefficient for the heater and positioner should be evaluated first. This is through setting $I_H = 1A$, $I_P = 0A$ and $I_H = 1A$, $I_P = 0A$ in the COMSOL model and using the following heat balance equation,

$$G_HI_H^2 + GP_I_P^2 = q_{avg}A$$  \hspace{1cm} (4.1)

where, $q_{avg}$ is the heat flux averaged over the surface calculated with COMSOL.

Next, according to equation 2.17 and 2.18, for a certain modulation frequency with small temperature modulation, $\Delta P_{av}$, which scales with $I_\omega^2$, is proportional to $\Delta T_{av}$ and $P_\omega$, which scales with $I_\omega I_H$, is proportional to $T_\omega$. Thus, true values for $I_{H_0}$, $I_\omega$ and $I_{P_0}$ can be calculated based on a test run with an arbitrary initial guess. By doing this, the current modulation in the experiment is determined: $I_{H_0} = 56.5A$, $I_\omega = 15A$ and $I_{P_0} = 295.3A$ (Figure 4.5).
The analytical solution dictates that the accuracy of $c_p$ measurement is determined by Bi number. The lower the Bi is, the more accurate $c_p$ measurement would be at isothermal modulation frequency. So, firstly, verification of this condition ($Bi < 0.01$) as listed in section 2.3.3 is performed.

To verify condition (i), which states that the temperature response on the poles and equator of the sample follow a pure exponential decay and have the same average increase, a step change was imposed to the heater current. Figure 4.2 shows the temperature change measured on the zenith and equator, respectively. First order decay curve fits to the original data curve and gives $\tau_1 = 14.4s$. The temperature change measured at these two positions is also very close.

![Figure 4.2. Temperature change at zenith and equator after step change in heater current. The fitted first order exponential decay curve cannot be discerned from the original data curve.](image)

To verify condition (ii): at isothermal modulation frequency $\omega_{max}$, the amplitude of the stationary temperature modulation at the poles and equator should agree with each other to 2% and $\phi_S(\omega_{max}) = -\pi/2$, power modulation at different frequencies was modeled. Figure 4.3 shows the dependence of $\phi_S$ on $\omega$. The $\omega_{max}$ is determined
to be 0.83 rads$^{-1}$. At this frequency, the polar and equator temperature response are $\Delta T_S = 6.4K$ and $\Delta T_H = 6.6K$, respectively. The difference, 2.8%, is slightly larger than the 2% criterion indicating that current Bi number might be over the isothermal modulation limit.

\[ \Delta T_S = 6.4K \quad \text{and} \quad \Delta T_H = 6.6K \]

\[ \text{Difference} = 2.8\% \]

\[ \text{Current Bi number might be over the isothermal modulation limit.} \]

**Figure 4.3.** \( \phi_S \) versus \( \omega \) for 10mm diameter solid Nb sample.

With \( \phi_S \) known, \( \lambda_2 \) and thus Bi can be calculated with equations 2.20 and 2.15. Figure 4.4 plots absolute value of \( \lambda_2 \) and \( Bi \). A similar pattern is observed for these curves. They are both weak functions of \( \omega \) at \( \omega > \omega_{max} \) but changes drastically at \( \omega < \omega_{max} \). This characteristic can be attributed to the influence of frequency on relaxation of thermal gradient due to modulated part of heat input. At the high frequency end, the internal flow pattern and thus heat transfer rate is well defined, so that \( \tau_2 \), thus \( Bi \), is relatively independent of \( \omega \). At low frequency end, the relaxation time of thermal gradient is effectively the modulation period. Therefore, as \( \omega \) gets smaller, both \( \tau_2 \) and Bi increases. For the frequency used in the experiment, \( Bi = 0.0073 \) which is smaller than 0.01, so that condition (iii) \( (Bi \leq 0.01) \) is also confirmed.

Next, the experiment is simulated with aforesaid current modulation. The reported time temperature curve is replicated perfectly with the model (Figure [?]).
According to equation 2.18, $c_p$ is calculated to be 349.4 J/KgK, which agrees with the experimental result in given uncertainty and is 2.3% larger than the value input into the model. The source of this difference is going to be discussed in the following section.

4.3 Utility of EML-MC for $c_p$ Measurement at Different Bi

Back to the definition, $Bi = \frac{hL}{k}$ is proportional to the characteristic length $L_C$, which is a strong function of the dimension of the sample. Hence, changing sample size would change Bi. In reality, the size of the sample amendable to EML process is limited due to manufacturing, dimensions of the apparatus, etc. However, with numerical model, the same sample with different sizes can be modeled and $c_p$ measurement at different Bi number can be studied.

We start off with the original Nb model and scale it by $A = \frac{R'}{R}$ (R’ is the new radius) times. Table 4.3 summarizes the dependence of characteristic values of EML-MC according to the analytical solution. In order to make sure the stretching of the model do not affect the physics, which is essentially the temperature distribution

Figure 4.4. Absolute value of $\lambda_2$ (blue) and Bi (red) versus $\omega$ plot.
Figure 4.5. Numerically recovered experimental time-temperature curve for $c_p$ measurement of solid Nb sample at 1840K.

Table 4.3. Change of characteristic values of EML-MC under stretching.

<table>
<thead>
<tr>
<th>Original Sample</th>
<th>$P(t)$</th>
<th>$\lambda_1$</th>
<th>$\lambda_2$</th>
<th>Bi</th>
<th>$\omega_{max}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stretched Sample</td>
<td>$A^3 \cdot P(t)$</td>
<td>$\frac{1}{A} \cdot \lambda_1$</td>
<td>$\frac{1}{A^2} \cdot \lambda_2$</td>
<td>$A \cdot Bi$</td>
<td>$\frac{1}{A^{3/2}} \omega_{max}$</td>
</tr>
</tbody>
</table>
inside of the solid sample, the original heating distribution is scaled corresponding to the change in size and mapped into the new sample,

\[ P(t)'(x, y) = \frac{P(t)}{A} \left( \frac{x}{A}, \frac{y}{A} \right) \] (4.2)

where, \( P(t)' \) is the new heating input.

Figure 4.6 plots characteristic parameters of EML-MC at different scalings based on both the analytical expressions and the simulation. These two sets of values agree well each other which implies that the size dependence of these quantities from analytical solutions is pretty accurate when the stretching is not very big (10 times smaller/larger than the original sample).

**Figure 4.6.** Based on the original Nb model, characteristic parameters of EML-MC is plotted at different scaling. Solid lines are predictions from the analytical expressions, dashed line are obtained from the simulation.

Table 4.4 characterizes \( c_p \) measurements at different Bi numbers and figure 4.7 plots the corresponding correction functions \( f_S \) and \( f_H \).
Figure 4.7. Correction functions $f_S$ (solid lines) and $f_H$ (dash lines) plots at different Bi numbers obtained through stretching the original model for solid Nb.
Table 4.4. Simulation results for $c_p$ measurement at different Bi.

<table>
<thead>
<tr>
<th>Scaling Bi at $\omega_{max}$</th>
<th>$\omega_{max}$ (rads⁻¹)</th>
<th>$\omega_{iso}$ range (rads⁻¹)</th>
<th>$c_p(S)$ at $\omega_{max}$ (J/kgK)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1X</td>
<td>0.007</td>
<td>0.834</td>
<td>0.38-1.9</td>
<td>348.3</td>
</tr>
<tr>
<td>0.5X</td>
<td>0.0034</td>
<td>2.36</td>
<td>0.63-9.4</td>
<td>344.2</td>
</tr>
<tr>
<td>0.1X</td>
<td>0.00066</td>
<td>26.4</td>
<td>2.8-251</td>
<td>341.9</td>
</tr>
<tr>
<td>5X</td>
<td>0.036</td>
<td>0.0746</td>
<td>N/A</td>
<td>377.1</td>
</tr>
<tr>
<td>10X</td>
<td>0.072</td>
<td>0.0264</td>
<td>N/A</td>
<td>414.7</td>
</tr>
</tbody>
</table>

The simulation results generally uphold the insights derived from the coupled heat flow model. At low Bi end (Figure 4.7 (a)), isothermal modulation range increases as Bi decreases and the most accurate $c_p$ measurement is obtained at $\omega_{max}$ with the associated error showing the same trend as Bi. However, it is observed that the Bi limit for isothermal modulation ($|1 - f_S(\omega_{max}, \lambda_1, \lambda_2)| \leq 10^{-2}$) is smaller than what has been reported by Wunderlich, et al. [102]. Our simulations show that the isothermal modulation is not accessible for Bi larger than 0.007. This difference might come from the approximated expression of $k_c$ adopted by Wunderlich, et al., in evaluating Bi.

At high Bi end, isothermal modulation range decreases rapidly. For Bi = 0.35 and 0.07, even at the isothermal modulation frequency, $f_S$ is still not close to 1 indicating large errors in $c_p$ measurement based on $\Delta T_\omega(S)$ (Figure 4.7 (b)). The analytical solution suggests that $c_p$ can be measured based on the evaluation of $f_H$ (Equation 2.21). Since $\lambda_1$, $\lambda_2$ and $c_4$ are all available from measurements of $\phi_S$ and $\phi_H$ using equation 2.20 and 2.22. The crux of this method then lies on the determination of $g_H$ which represents the fraction of the directly heated volume in the coupled heat flow model. With $f_H$ been determined numerically (Figure 4.7), $g_H$ can be calculated using equation 2.21. Figure 4.8 plots $g_H$ verse $\omega$ for the solid Nb sample at 1840K.

$g_H$ displays a minimum at $\omega_{max}$ and increases as modulation frequency deviates from that particular value. To explain this trend, one should recognize that, $g_H$
Figure 4.8. Fraction heated ($g_H$) versus modulation frequency $\omega$ plot for the original Nb model.

originates from the highly nonuniform character of E.M. heating. When Bi is small, which is generally true for the current research, the two distinct heating zones can be treated as two isothermal volumes as in the coupled heat flow model. However, whether the heating field or the temperature field changes continuously, that is to say that, essentially, $g_H$ is just an approximation of the fraction of the volume with uniform temperature under 0th order approximation to the temperature distribution within the sample. Given that, two conclusions can be drawn. Firstly, the increase of $g_H$ for $\omega > \omega_{\text{max}}$ can be attributed to the finite thermal conductivity of the material which limits the amount of heat that can be removed out of the directly heated zone. While for $\omega < \omega_{\text{max}}$, the increase in $g_H$ can be explained by thermal diffusion during longer modulation period. Secondly, as a 0th order model, $g_H$ is a gross simplification created to help simplify the analysis of the problem. Trying to evaluate $g_H$ is impractical except from the full internal temperature distribution which requires
a numerical or analytical solution of heat flow, that is, for larger Bi, $g_H$ no longer provides any simplification to the solution of the heat flow problem.

Although the attempt to measure $c_p$ through $g_H$ is not successful, the simulation results indicates that good estimation of $c_p$ can still be obtained at $\omega_{\text{max}}$ without using $f_H$ (table 4.5). It is also observed that, for large samples, Bi and $\omega_{\text{max}}$ do not scale with the proportionality listed in table 4.3 4.9, which indicates that $\lambda_2$, Bi and essentially $k_c$ is not a simple first order function of the radius of the sample, but rather having a more complicated (higher order) dependence on it.

**Table 4.5.** $c_p$ measurement at large Bi numbers with $\Delta T_s(H)$.

<table>
<thead>
<tr>
<th>Scaling</th>
<th>$\text{Bi at } \omega_{\text{max}}$</th>
<th>$\omega_{\text{max}}$ (rads$^{-1}$)</th>
<th>$c_p(s)$ ($J/kgK$)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1X</td>
<td>0.007</td>
<td>8.34E-1</td>
<td>337.9</td>
<td>-1%</td>
</tr>
<tr>
<td>10X</td>
<td>0.07</td>
<td>2.46E-2</td>
<td>328.7</td>
<td>-3.7%</td>
</tr>
<tr>
<td>20X</td>
<td>0.13</td>
<td>8.49E-2</td>
<td>328.3</td>
<td>-3.8%</td>
</tr>
<tr>
<td>70X</td>
<td>0.35</td>
<td>1.27E-3</td>
<td>351.8</td>
<td>3%</td>
</tr>
</tbody>
</table>

**Figure 4.9.** For larger samples, Bi and $\omega_{\text{max}}$ does not follow the size dependence defined by the analytical solutions.
4.4 Conclusions

This chapter presents simulation results for \( c_p \) measurement at different Bi numbers based on the reported experiment on solid Nb at 1840K. The findings may be summarized as follows:

(a) The analytical solutions and operational principles derived from the coupled heat flow model are accurate for \( c_p \) measurement of solid materials at small Bi numbers.

(b) Isothermal modulation is not available for \( Bi \geq 0.007 \).

(c) \( g_H \) represents the fraction of the heated isothermal volume under zeroth order approximation to the temperature distribution. Evaluation of \( g_H \) is impractical and cannot be used in accurate determination of \( c_p \) in the high Bi range.

(d) However, \( c_p \) measurements with error < 5% can be obtained by using the amplitude of the equatorial temperature fluctuation \( \Delta T_o(H) \) up to the largest sample simulated: \( Bi = 0.35 \).
CHAPTER 5

NUMERICAL STUDY OF THERMAL CONDUCTIVITY MEASUREMENTS WITH EML-MC

Theoretically, $k$ can be solved from internal heat transfer coefficient $k_c$ which is obtained through measuring internal relaxation time $\tau_2$ (equation 2.15, 2.14 and 2.3). However, there are two major difficulties with the implementation of this method: the lack of accurate analytical expression for $k_c$ and the determination of convective contribution in the measured $k_c$ for liquid materials. Computational simulation provides another means for accurate determination of $k$. Supposing all other thermophysical properties of the test material are known, $k$ can then be treated as a free parameter and determined by reproducing the EML-MC experiment, i.e. recreating the same temperature response on the sample surface, using numerical simulation.

In light of this idea, this chapter presents a case study of $k$ measurement of a Zirconium based metallic glass forming alloy, $Zr_{65}Al_{17}Cu_{17.5}Ni_{10}$. Microgravity EML-MC based thermal measurement of this material is conducted during Spacelab mission MSL-1. Using numerical simulation, $k$ and measurement error of the analytical $k$ are determined at both solid and liquid phase. Hypothetical computational experiments are designed and implemented to examine the applicability of current analytical expression of $k_c$ derived from the heat transfer model for solid sample. For the liquid sample, the error in the measured $k$ from forced E.M. convection is quantified under different scenarios. The possibility of using CFD to provide insights and guidance to future $k$ measurements of liquid materials is demonstrated from analyzing the results of simulation based virtual experiments. Lastly, a rigorous uncertainly analysis following the Guide to the Expression of Uncertainty in Measurement (GUM) for $k$
measurement of liquid materials is presented and practical recommendations for more accurate k measurements are provided.

5.1 EML-MC on Zr Alloy

Microgravity EML-MC experiments are performed on 4mm radius Zr$_{65}$Al$_{17.5}$Cu$_{17.5}$Ni$_{10}$ alloy samples during Spacelab mission MSL-1. The coil geometry are shown in figure 2.1 (b). The heater current has a frequency of 350kHz and the positioner 160kHz. Table 5.1 lists some of the experimental data reported by Wunderlich, et al., ([97]) at both solid and liquid state. Both experiments are performed in power modulation mode which eliminates the transient response of $P_{av}$ (Figure 5.1). The test material’s properties are listed in table 3.4 and 5.2.

![Image of EML-MC experiment](image_url)

**Figure 5.1.** EML-MC operating at power mode for thermal measurement of under-cooled liquid Zr$_{65}$Al$_{17.5}$Cu$_{17.5}$Ni$_{10}$ alloy [97].

5.2 k Measurement of Solids

The temperature response of the sample is determined by the internal heat and fluid flow, which can be accurately simulated with the numerical model by inputing the correct materials properties and current modulation. The only unknown property
Table 5.1. Microgravity EML-MC of $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ alloy.

<table>
<thead>
<tr>
<th>$(I_{H_0})^2(A^2)$</th>
<th>$I_P$(A)</th>
<th>$L_s/I_H$</th>
<th>$T_0$(K)</th>
<th>$f$(Hz)</th>
<th>$\phi_S$(deg)</th>
<th>$\tau_2$(s)</th>
<th>Measured k (W/mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>705</td>
<td>160.4</td>
<td>0.6</td>
<td>1033*</td>
<td>0.16</td>
<td>99.8</td>
<td>0.19</td>
<td>21</td>
</tr>
<tr>
<td>676</td>
<td>160.4</td>
<td>0.6</td>
<td>1024 l</td>
<td>0.16</td>
<td>100</td>
<td>0.2</td>
<td>31.2</td>
</tr>
</tbody>
</table>

* Superscripts s and l refer to the solid and liquid phases, respectively.

Table 5.2. Properties of liquid $Zr_{65}Al_{7.5}Cu_{17.5}Ni_{10}$ alloy at 1024K.

<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius</td>
<td>R</td>
<td>4.035mm</td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>$\rho$</td>
<td>6650Kg/m$^3$</td>
<td></td>
</tr>
<tr>
<td>Electrical Conductivity</td>
<td>$\sigma_{el}$</td>
<td>$6.54 \times 10^5$(Ωm)$^{-1}$</td>
<td>[97]</td>
</tr>
<tr>
<td>Total hemispherical emissivity</td>
<td>$\varepsilon$</td>
<td>0.24</td>
<td>[101]</td>
</tr>
<tr>
<td>Specific heat capacity</td>
<td>$c_p$</td>
<td>569.5J/KgK</td>
<td>[101]</td>
</tr>
<tr>
<td>Viscosity</td>
<td>$\mu$</td>
<td>0.27Pa⋅s</td>
<td>[13]</td>
</tr>
</tbody>
</table>

here is $k$. So, by simulating the experimental temperature response of the sample with $k$ as a free parameter, a numerical $k$ can be determined.

Based on this idea, a series of numerical simulations is performed with different $k$ values to match the experimental data for the solid Zr-alloy at 1033K. Figure 5.2 plots the dependence of $\phi_S$ on $k$. The numerical $k$ is determined to be 20.4 W/mK, which agrees well to $k = 23$W/mK obtained from using Wiedemann-Franz law with independently measured electrical resistivity of 1150Ωm.

The $k$ reported is 21W/mK, which is about 4% larger than the value obtained by our numerical analysis. Here, we introduce a new quantity that characterizes the error in the measured apparent $k$ using analytical expression of $k_e$ versus numerically determined $k$: correction factor (CF). CF is defined as,

$$CF = \frac{\text{Analytical } k}{\text{Numerical } k}$$ (5.1)
The measured analytical $k$ reported by Wunderlich, et al., is calculated using equation 2.27.

$$k_c = \frac{4}{3} \pi^3 R k$$  \hspace{1cm} (5.2)

This analytical expression is derived from an ideal heat transfer model for solid spherical samples: uniform surface temperature and spherical symmetric distributed sinusoidal heat input [16]. Despite the difference in the theoretical models, previous ground based EML-MC experiments on Nb has confirmed that $\tau_2$, which is essentially $k_c$, from the heat transfer model agrees to better than 10% with this expression [102]. Wunderlich, et al., later proposed a more accurate expression for $k_c$ as seen in equation 2.3. In this version, $\gamma$ and skin depth $\delta$ are two geometric factors that takes into account the non-spherical symmetric distribution of heating power and skin depth. Unfortunately, it appears that the addition of these two extra factor are purely phenomenological. Plus, the analytical expressions for $\gamma$ is not given. Determin
nation of this value relies solely on calibration experiments, which is usually tedious considering the already complex experimental procedures.

In our case, for the solid Zr-alloy, $CF = 1.04$ confirms the applicability of equation 2.27. But the next question is what is the dependence of $CF$ on different measurement condition. It is known from equation 2.3 that $k_c$ is a function of radius $R$, skin depth $\delta$ and geometric factor $\gamma$, which is dependent on the non-spherical symmetric distribution of heating input. In EML-MC, heater and positioner will produce two different skin depths $\delta_H$ and $\delta_P$ depending on their individual modulation frequency $\omega_H$ and $\omega_P$. The dependence of $\delta$ in equation 2.27 on $\delta_H$ and $\delta_P$ is unclear. On the other hand, $\gamma$ has an even more complex dependence on different parameters. These parameters include $\omega_H$ and $\omega_S$, the ratio of power input from heater versus positioner ($\frac{P_H}{P_P}$), sample radius, $c_p$, k and hemispherical emissivity $\varepsilon$ and, for liquid samples, viscosity. To thoroughly understand the dependence of $k_c$ on these parameters, a total of $5^9 = 1953125$ experiments are needed assuming each of the individual parameter has five possible values. Given the limited computational resource available to current research, a simpler approach is chosen. Instead of exploring all combinations, only one individual parameter is examined at a time. Also, the research scope is limited to the particular material ($Zr_{65}Al_{17.5}Cu_{17.5}Ni_{10}$ alloy), coil geometry (MSL-1 TEMPUS) and frequencies ($\omega_H = 350kHz$ and $\omega_P = 160kHz$). Lastly, considering the skin depth is proportional to $\frac{1}{\sqrt{\sigma \omega}}$, varying electrical conductivity $\sigma$ is equivalent to varying $\omega$ in term of studying skin depth. In summary, the individual parameters studied are $R$, $\frac{P_H}{P_P}$, electrical conductivity $\sigma$ of the material. Table 5.3 lists specific values of these parameters that is used to study dependence of $CF$.

For each hypothetical experiment, operating currents are scaled to maintain the original temperature, i.e. 1033K on the pole. For all the hypothetical experiments planned, $Bi$ is generally smaller than 0.01. So the difference in the total heating of each experiment after scaling is minimal and would not affect the significance of
Table 5.3. Variable values to be tested for \( k_c \)

<table>
<thead>
<tr>
<th>Independent variable</th>
<th>( R ) (mm)</th>
<th>( \frac{P_H}{P_P} )</th>
<th>Electrical Conductivity ((Ω·m)(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original</td>
<td>4</td>
<td>0.9</td>
<td>( 8.7 \times 10^5 )</td>
</tr>
<tr>
<td>Value 1</td>
<td>2</td>
<td>0.1</td>
<td>( 0.25 \times 8.7 \times 10^5 )</td>
</tr>
<tr>
<td>Value 2</td>
<td>3</td>
<td>10</td>
<td>( 4 \times 8.7 \times 10^5 )</td>
</tr>
<tr>
<td>Value 3</td>
<td>5</td>
<td>100</td>
<td>( 9 \times 8.7 \times 10^5 )</td>
</tr>
<tr>
<td>Value 4</td>
<td>6</td>
<td>1000</td>
<td>( 16 \times 8.7 \times 10^5 )</td>
</tr>
</tbody>
</table>

Current research on \( k \) measurement. The current modulation amplitude is maintained at \( \frac{I}{I_{H_0}} = 0.6 \), so that the effect of the variation in the current modulation can be eliminated. \( \phi_0 \) is chosen to be \(-90^\circ\) to be consistent with the experiment. \( \lambda_1 \) is determined by fitting first order exponential decay curve to the free cooling curve after step-change in heater current. \( \lambda_2 \) is determined by identifying the isothermal frequency \( \omega_{\text{max}} \) using bisection algorithm and applying the relationship \( \omega_{\text{max}} = \sqrt{\lambda_1 \lambda_2} \) (equation 2.26).

Figure 5.3 plots the dependence of CF on each individual parameter. The red dots correspond to original EML-MC experiment on Zr-alloy. The others data points are from hypothetical computational experiments. It can be seen that, from (a), CF, which is effectively the measurement error with equation 2.27, decreases monotonically with skin depth. There is a change in the slope of the curve near skin depth equal to about half radius of the sample. CF is a stronger function of skin depth before that point than after. From (b), CF is a weak function of the heating ratio \( \left( \frac{P_H}{P_P} \right) \). \( k \) measurement under heater dominated heating \( \left( \frac{P_H}{P_P} > 1 \right) \) is more accurate than positioner dominated heating \( \left( \frac{P_H}{P_P} < 1 \right) \), but only by about 0.5%. From (c), CF displays a monotonical relationship with radius of the sample. Thus, smaller samples should be used to measure \( k \) of the Zr-alloy with EML-MC at 1033K. In generally, equation 2.27 is a good approximation for the internal heat transfer coefficient of solid Zr-alloy at 1033K \( (CF < 1.1) \). Using larger skin depth, larger heater to positioner...
heating ratio and smaller sample size would result into better measurement accuracy.

5.3 k Measurement of Liquids

Similar to k measurement of solids, a series of numerical simulations is performed to match the experimental data for the undercooled liquid Zr-alloy at 1024K. Figure 5.4 plots the dependence of $\phi_S$ on k. By interpolation, k is determined to be 28 W/mK. The CF is calculated to be 1.11, indicating that there is a 11% error in the measured apparent k. Using Wiedemann-Franz law and independently measured electrical resistivity of 1530Ωm ([101]), k is determined to be 16.4 W/mK, which is significantly smaller than the k value determined using numerical simulation and the experimentally measured analytical k. The discrepancy may be a result of the limited temperature resolution of the pyrometer used in the experiment. The effect of temperature measurement accuracy on k will be discussed in the following section.

In order to provide insights for future k measurement of liquid materials, it is useful to study the dependence of measurement error, or CF, on different measurement conditions and also for liquid materials, viscosity. Using material properties of liquid Zr-alloy at 1024K, figure 5.5 plots CF against viscosity under various designed conditions. Generally speaking, due to the negative correlation between viscosity and forced E.M. convection, small viscosity results into large errors in the measured analytical k, or large CF. However, this is not true for all cases. For the current case tested, liquid Zr-alloy, four zones can be distinguished in terms of CF. The first zone is where $\mu > 1 Pa\cdot s$. In this range, CF is almost constant and is very close to 1. Fluid flow has little contribution to the internal heat transfer. All the measurement error in k results from systematic error in equation 2.27 and is smaller than 10%. The second zone is where $1 Pa\cdot s > \mu > 0.1 Pa\cdot s$. In this regime, measurement error due to
Figure 5.3. Dependence of CF on skin depth ($\delta$), heating ratio ($\frac{P_{H}}{P_{P}}$) and radius (R) for solid Zr-alloy at 1033K. Dashed lines correspond to CF=1. Offset between the solid curves and dashed lines indicates the systematic error in the $k_c$ expression proposed by Fetch and Johnson (equation 2.27).
forced E.M. convection has a comparable magnitude to systematic error in equation 2.27. And the convective contribution follows a linear relationship with respect to viscosity up to a maximum CF of 1.35. In the zone where $0.1 Pa \cdot s > \mu > 0.02 Pa \cdot s$, the measurement error is dominated by forced convection. From figure 5.5 (a) and (c), it can be seen that similar to the dependence of CF for solids, small skin depth and large sample size result into larger convective error for the same viscosity. From 5.5 (b), it is observed that heater dominated heating ($\frac{P_H}{P_P} > 1$) tends to have smaller convective error than positioner dominated heating ($\frac{P_H}{P_P} < 1$).

The last zone is where $\mu < 0.02 Pa \cdot s$. In this regime, CF is strongly affected by the internal flow field. Since the flow field is a complex function of the test material’s size and properties, EML coilset and current modulation, small difference in each of these individual variables could lead to totally different flow flows and also different CFs. Consequently, the change of CF in this regime displace a very complex behavior. Figure 5.6 plots different flow fields for the liquid Zr-alloy at 1024K with the same $0.01 Pa \cdot s$ viscosity and different radii.

Figure 5.4. Dependence of $\phi_S$ on k for 1024K liquid Zr-alloy.
Figure 5.5. Dependence of CF on viscosity for different skin depths ($\delta$), heating ratios ($\frac{P_{H}}{P_{p}}$) and radii (R) for liquid Zr-alloy at 1024K.
Figure 5.6. Different flow fields for liquid Zr-alloy at 1024K with 0.01 Pa·s viscosity and different radii.
5.4 Uncertainty Analysis

One of the major challenges with high temperature measurements is the uncertainty. In order to better leverage computational tools for the planning of future k measurements, it is important to understand how uncertainties from different sources propagate through measurements and simulation and affect the predicted CF. In this section, the uncertainties involved in the predicted CF is evaluated according to the Evaluation of measurement data - Guide to the expression of uncertainty in measurement, or GUM analysis, for short [47]. GUM analysis established a standard and systematic way for calculating and expressing uncertainties in measurement. Typical GUM analysis can be summarized as follows: 1) Establish an analytical relationship between the measurand and the input quantities. 2) Determine the estimated value and standard uncertainty for each of the input quantities. And if any of the input quantities are correlated, evaluate the covariance too. 3) Determine the estimated value of the measurand and its standard uncertainty using the aforementioned analytical expression. 4) Report the result of measurement together with its uncertainty using standard formats published in the guide.

Following is a standard GUM analysis for CF of the original liquid Zr-alloy at 1024K with different viscosities (Figure 5.7). The quantity that is of interest, or the measurand, is CF. It represents the error level of k measurement at different experimental settings and at different viscosities. The individual quantities that could affect CF are total hemispherical emissivity, viscosity, electrical conductivity, coil frequencies of heater and positioner, modulation current, temperature, sample radius, density and mass. Table 5.4 lists typical values for these uncertainty sources for current EML-MC based measurements.

To establish a relationship of CF with these different error sources, it is useful to go back to the definition of CF (equation 5.1). Assuming the numerical k determined in section 5.3 is correct. Then, the error in CF is effectively the error in the measured
Figure 5.7. CF curve for 1024K Zr-alloy at different viscosities.

Table 5.4. Error sources and their typical values from EML-MC measurements

<table>
<thead>
<tr>
<th>Source</th>
<th>Uncertainty</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>total hemispherical emissivity ($\varepsilon$)</td>
<td>4%</td>
<td>[41]</td>
</tr>
<tr>
<td>viscosity ($\mu$)</td>
<td>25%</td>
<td>[40]</td>
</tr>
<tr>
<td>electrical conductivity ($\sigma_e$)</td>
<td>0.5%</td>
<td>[25]</td>
</tr>
<tr>
<td>coil frequencies ($\omega_H, \omega_P$)</td>
<td>0.1%</td>
<td>[41]</td>
</tr>
<tr>
<td>modulation current ($I_H, I_P, I_\omega$)</td>
<td>0.5%</td>
<td>[41]</td>
</tr>
<tr>
<td>sample radius (R)</td>
<td>0.033%</td>
<td>[41]</td>
</tr>
<tr>
<td>sample density ($\rho$)</td>
<td>0.1%</td>
<td>[12]</td>
</tr>
<tr>
<td>sample mass</td>
<td>0.005%</td>
<td>[41]</td>
</tr>
<tr>
<td>temperature($T_S$)</td>
<td>accuracy: 2K~5K</td>
<td>[41]</td>
</tr>
<tr>
<td></td>
<td>precision: 0.1K</td>
<td>[41]</td>
</tr>
</tbody>
</table>
analytical $k$. Analytical $k$ in the experiment is obtained by determining $\lambda_2$ (equation 2.20) through measuring phase lag $\phi_S$ and using equation 2.27. $\lambda_1$ complies with the following analytical expression based on the heat transfer model,

$$\lambda_1 = \frac{k_r}{mc_p} = \frac{12\varepsilon T_0^3}{R \rho c_p} \quad (5.3)$$

The error in emissivity affects the analytical $k$ through $\lambda_1$. $\lambda_1$ is proportional to $\varepsilon$. The uncertainty in CF, or equivalently $\lambda_2$ is inversely proportional to the error in $\lambda_1$ according to $\omega_{\text{max}} = \sqrt{\lambda_1/\lambda_2}$. Thus, a uncertainty of 4% in emissivity would also resulting into a 4% uncertainty in measure $k$, or an equivalent CF from 0.96~1.04. This is about the same magnitude as CF in zone 1 and 2. Thus, in order to use CF in large viscosity range, it is important to improve the measurement accuracy in emissivity. However, since the total hemispherical emissivity changes slowly with temperature, the method can still give very precise information about relative changes in $k$, even if the accuracy of that $k$ value is limited by the accuracy of the emissivity value.

The uncertainty in permeability measurement is zero because the EML-MC experiments are conducted at a temperature higher than the Curie temperature of the Zr-alloy. So, permeability measurement does not contribute to the uncertainty of CF. Uncertainty in viscosity measurement can be directedly read off the original curve. Table 5.5 lists the uncertainty in CF from viscosity for the original 1024K Zr-alloy CF curve at different viscosities. The measurement uncertainty in viscosity generally has a small impact on CF within zones 1 and 2. In zones 3 and 4, better viscosity measurement is required for the accurate predictions of CF.

Electrical conductivity affects the problem through skin depth, E.M. force and power input. For Zr-alloy at 1024K, the radius/skin depth ratio is about 4. According to reference [42], at this range, E.M. force is independent of $\sigma_e$. E.M. power affects CF through $T_0$. However, for constant temperature experiments, there is no contribution
Table 5.5. Uncertainty in CF due to uncertainty in viscosity measurement

<table>
<thead>
<tr>
<th>Viscosity ($Pa \cdot s$)</th>
<th>10</th>
<th>1</th>
<th>0.1</th>
<th>0.05</th>
<th>0.03</th>
<th>0.02</th>
<th>0.01</th>
</tr>
</thead>
<tbody>
<tr>
<td>From</td>
<td>0.06%</td>
<td>0.3%</td>
<td>4%</td>
<td>13%</td>
<td>23%</td>
<td>9%</td>
<td>N/A</td>
</tr>
<tr>
<td>To</td>
<td>N/A</td>
<td>-0.4%</td>
<td>-1.5%</td>
<td>-7%</td>
<td>-11%</td>
<td>-14%</td>
<td>-5%</td>
</tr>
</tbody>
</table>

from $\sigma_e$ to the uncertainty of CF through E.M. power. Lastly, the dependence of CF on $\sigma_e$ through skin depth can be calculated from figure 5.5 (a). Table 5.6 lists the uncertainty in CF from $\sigma_e$ for the original 1024K Zr-alloy CF curve at different viscosities. The measurement uncertainty in electrical conductivity generally has a small impact on CF.

Table 5.6. Uncertainty in CF due to uncertainty in electrical conductivity measurement

<table>
<thead>
<tr>
<th>Viscosity ($Pa \cdot s$)</th>
<th>10</th>
<th>1</th>
<th>0.1</th>
<th>0.05</th>
<th>0.03</th>
<th>0.02</th>
<th>0.01</th>
</tr>
</thead>
<tbody>
<tr>
<td>From</td>
<td>0.004%</td>
<td>0.005%</td>
<td>0.026%</td>
<td>0.06%</td>
<td>0.09%</td>
<td>0.1%</td>
<td>0.35%</td>
</tr>
<tr>
<td>To</td>
<td>-0.006%</td>
<td>-0.007%</td>
<td>-0.023%</td>
<td>-0.06%</td>
<td>-0.11%</td>
<td>-0.14%</td>
<td>-0.054%</td>
</tr>
</tbody>
</table>

Coil frequency affects the measure $k$ through E.M. force, power and skin depth. For the same reason, the contribution to CF from $\omega_H, \omega_P$ is only through skin depth. Table 5.7 lists the uncertainty in CF from coil frequency for the original 1024K Zr-alloy CF curve at different viscosities. Similar to $\sigma_e$, the measurement uncertainty in coil frequency has little influence on CF.

Table 5.7. Uncertainty in CF due to uncertainty in coil frequency measurement

<table>
<thead>
<tr>
<th>Viscosity ($Pa \cdot s$)</th>
<th>10</th>
<th>1</th>
<th>0.1</th>
<th>0.05</th>
<th>0.03</th>
<th>0.02</th>
<th>0.01</th>
</tr>
</thead>
<tbody>
<tr>
<td>From</td>
<td>0.0008%</td>
<td>0.001%</td>
<td>0.005%</td>
<td>0.01%</td>
<td>0.02%</td>
<td>0.02%</td>
<td>0.07%</td>
</tr>
<tr>
<td>To</td>
<td>-0.001%</td>
<td>-0.001%</td>
<td>-0.005%</td>
<td>-0.01%</td>
<td>-0.02%</td>
<td>-0.03%</td>
<td>-0.01%</td>
</tr>
</tbody>
</table>

85
Modulation currents affect CF through E.M. Force and power. E.M. Force is proportional to the square to modulation current. So, uncertainty in E.M. force is twice the uncertainty in current, which is 1%. Since at low Reynolds number limit, E.M. force is proportional to viscosity at given flow velocity. 1% uncertainty in E.M. force is equivalent to 1% uncertainty in viscosity. Considering also that effect of modulation current uncertainty on E.M. power is zero due to the constant temperature experiment assumption. The lumped uncertainty in CF on modulation current can be calculated from the original curve. Table 5.8 lists the uncertainty in CF from modulation current for the original 1024K Zr-alloy CF curve at different viscosities.

Table 5.8. Uncertainty in CF due to uncertainty in modulation current measurement

<table>
<thead>
<tr>
<th>Viscosity (Pa⋅s)</th>
<th>10</th>
<th>1</th>
<th>0.1</th>
<th>0.05</th>
<th>0.03</th>
<th>0.02</th>
<th>0.01</th>
</tr>
</thead>
<tbody>
<tr>
<td>From</td>
<td>0.0024%</td>
<td>0.012%</td>
<td>0.16%</td>
<td>0.52%</td>
<td>0.92%</td>
<td>0.36%</td>
<td>N/A</td>
</tr>
<tr>
<td>To</td>
<td>N/A</td>
<td>-0.016%</td>
<td>-0.06%</td>
<td>-0.28%</td>
<td>-0.44%</td>
<td>-0.56%</td>
<td>-0.2%</td>
</tr>
</tbody>
</table>

Sample radius affects CF through both $\lambda_1$ and $\lambda_2$. $\lambda_1$ is inversely proportional to R. And since for a particular system, $\omega_{max}$ is constant and equal to $\sqrt{\lambda_1\lambda_2}$, so uncertainty in $\lambda_2$ also be proportional to the uncertainty in R. Also considering that k is proportional to $\lambda_2R^2$, so the uncertainty in CF should be proportional to 3 times of the uncertainty in R, which is about 1%.

Sample density affects CF through both $\lambda_1$ and $\lambda_2$. $\lambda_1$ is inversely proportional to $\rho$, so uncertainty in $\lambda_2$ should be proportional to the uncertainty in $\rho$. Also considering that k is proportional to $\lambda_2\rho$, so the uncertainty in CF should equals to twice of the uncertainty in $\rho$, which is 0.2%. Accuracy in the measurement of sample mass affects CF through both $\lambda_1$ and $\lambda_2$. $\lambda_1$ is inversely proportional to m, so uncertainty in $\lambda_2$ should be proportional to the uncertainty in m. Also considering
that \( k \) is proportional to \( \lambda_2 m \), so the uncertainty in CF is approximately twice the uncertainty in \( m \), which is about 0.01%.

Accuracy in the measurement of temperature affects CF through both \( \lambda_1 \). \( \lambda_1 \) is proportional to the cube of \( T_0 \), so uncertainty in \( \lambda_2 \), which is essentially analytical \( k \), should be three times of the uncertainty in \( T \), which is about 0.6\% \( \sim \) 1.5\%. The precision of the temperature measurement affects CF through the determination of the phase lag \( \phi_S \). \( \phi_S \) is determined by tracking the time difference between the peak or trough in the temperature signal and those in the current modulation. In current experiment, the modulation amplitude in heater current is 60\% and that results into a small temperature modulation response of about 1.4K. Given the current temperature measurement precision, it is really hard to determine the true peak or trough in the temperature signal. From numerical simulation, within the 0.1K range, \( \phi_S \) ranges from 80° to 120°. That corresponds to \( k \) ranging from 10.3W/mK to infinity, or CF ranging from 0.37 to infinity. Thus, in summary, raising measurement precision in temperature is the most important in terms of reducing error in CF.

5.5 Conclusions

In this chapter, the potential of \( k \) measurement for high temperature liquid materials using EML-MC are studied based on a case study on a bulk glass forming alloy Zr\(_{65}\)Al\(_{7.5}\)Cu\(_{17.5}\)Ni\(_{10}\). The main findings of this chapter may be summarized as follows:

1) Numerical \( k \) value of the Zr-alloy at both solid and liquid status is determined by recreating the EML-MC experiment using CFD. For the solid case, the numerically determined \( k \) is very close to the reported value, thus confirms the application of the simple analytical expression for \( k_c \). While for the liquid case, the determination of \( k \) confirms the feasibility of using CFD for measuring \( k \) of liquid materials.
2) Hypothetical experiments of k measurements using different combination of experimental parameters are designed and implemented using COMSOL. It is found that, for solids, small skin depth and large sample size lead to large measurement error in k. The dependence of k error on heating ratio is relatively small. In generally, with current k measuring technique, the error in k is smaller than 10%. For liquids, the general rules are very similar to that of solids. At the same viscosity level, small skin depth and large sample size lead to large measurement error in k. Variation in heating ratio has a relatively small impact on k error. However, it it noticed that measurement error of k in larger when positioner heating is dominant.

3) For the current case studied, four distinct zones in viscosity can be distinguished in terms of k measurement error. In zone 1 \((10 Pa \cdot s)\), k error is constant and results solely from the systematic error of the analytical expression of internal heat transfer coefficient \(k_c\). In zone 2 \((10 Pa \cdot s < \mu < 1 Pa \cdot s)\), k error follows a linear relation with viscosity in a log-log plot. In zone 3 \((1 Pa \cdot s < \mu < 0.1 Pa \cdot s)\), k error from force E.M. convection dominates over systematic error in \(k_c\). In zone 4 \((\mu < 0.1 Pa \cdot s)\), the change in k error doesn’t monotonically increase and it is greatly affected by the internal flow pattern.

4) Using methods of this chapter, range for k measurement is extended by 1.5 orders of magnitude in permissible viscosities. For lower viscosities, uncertainty in convection dominates the result. A uncertainty analysis following GUM is conducted. It is found that the biggest uncertainty source in CF is the measurement precision of temperature. All other parameters generally have small impact in predicted CF.
CHAPTER 6
CONCLUSIONS

Numerical simulation combined with electromagnetic levitation technique provides a means for accurate determination of thermophysical properties of high temperature materials in both solid and liquid status. In current research, numerical models of samples under EML process is developed and validated. EML-MC based $c_p$ and $k$ measurements of high temperature solid and liquid materials are simulated and studied. Major findings can be summarized as following:

For $c_p$ measurement of solid:

1) The analytical solutions and operational principles developed from simple heat transfer model are confirmed numerically.

2) Computational studies predicted a more conservative condition for isothermal modulation. It is found that isothermal modulation is not available for $Bi \geq 0.007$.

3) EML-MC pioneer Wunderlich, et al., proposed to use $g_H$ for the determination of $c_p$ at high Bi number regime. However, numerical simulation show that $g_H$ is a function of the modulation itself. Determination of $g_H$ requires knowledge of the detailed temperature distribution of the system. Moreover, there is no clear definition of $g_H$ from the 0th order heat transfer model. Using $g_H$ to calculate $c_p$ for high Bi numbers is not practical.

4) At $\omega_{max}$, $c_p$ can be determined by using equatorial temperature fluctuation with an error smaller than 5% up to the largest tested sample with Bi=0.35, which is 35 times larger than the originally reported Bi limit for ideal $c_p$ measurements.
For k measurement of liquids:

1) By combining CFD and EML-MC experiment, k can be accurately measured for high temperature materials at both solid and liquid state.

2) Based on a case study on bulk metallic glass-forming alloy Zr$_{65}$Al$_{7.5}$Cu$_{17.5}$Ni$_{10}$, it is found that for solid samples, small skin depth and large sample size lead to large measurement error in k. Heating ratio has a relatively small impact on the measurement of k. For liquid samples, the same rule is generally followed except that positioner dominated heating results into larger measurement error in k than heater dominated heating.

3) For k measurement of liquids, four distinct zones in viscosity can be distinguished in terms of k measurement error. In zone 1 ($1 Pa \cdot s < \mu$), k error is constant and results solely from the systematic error of the analytical expression of internal heat transfer coefficient $k_c$. In zone 2 ($1 Pa \cdot s > \mu > 1 Pa \cdot s$), k error follows a linear relation with viscosity in a log-log plot. In zone 3 ($0.1 Pa \cdot s > \mu > 0.02 Pa \cdot s$), k error from force E.M. convection dominates over systematic error in $k_c$. In zone 4 ($\mu < 0.02 Pa \cdot s$), the change in k displays complex behavior determined by the internal flow pattern.

4) Based on GUM uncertainty analysis, it is found that the largest uncertainty source for the determination of k is the measurement precision of temperature.
CHAPTER 7
FUTURE WORK

Potential future work for this study includes:

1) Detailed modeling of the thermal boundary. In the current research, thermal radiation and reflected energy from the peripheral apparatus: RF coils, sample holder and chamber, etc. was not considered. Also, sometimes in ground EMLs, gas cooling is used to control the temperature of the droplet. In order to better understand and improve this technique, these details should be considered in the future to improve the accuracy of the simulation.

2) Deformation of the sample. Under large heating or positioning currents, E.M. force can squeeze the sample into a spheroid in microgravity EMLs or a reversed droplet shape in terrestrial experiments [28]. Predictably, the change in the geometry might affect the internal fluid flow and eventually the temperature response. Hence, in order to simulate EML-MC with high fidelity, it would be beneficial to include this physics in the model in the future. For low melting samples, these distortions are small, but for high melting samples, the distortion can exceed 10%.

3) The EML-MC technique is essentially a complex multi-physics system. The only parameter, temperature, based on which thermophysical properties are measured, is actually affectly by everything involved in this system: coil geometry, coil frequency, heater/positioner current, modulation amplitude and frequency, materials properties. To complete understand the dependece of the behavior of thermal measurements with EML-MC on different parameters, a million to several tens of millions of simulation would be required. Due to limited resource, in current study, only some
of the major parameters are studied according to the simple $0^{th}$ order heat transfer model. In the future, in order to accommodate large computational needs and cut down simulation time, it is important to parameterize the whole simulation in terms of principle component and automate it using scripts and journals.

4) Lastly, current EML-MC method is developed based on a simple $0^{th}$ order heat transfer model. Though it has been proved accurate enough for most of scenarios in solid state, a more accurate theoretical model and corresponding analytical solutions for EML-MC are still needed to better understand and improve EML-MC.


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