Thermal Conductivity and Noise Attenuation in Aluminium Foams

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Preface

This dissertation is submitted for the degree of Master of Philosophy in Materials Modelling at the University of Cambridge. The research described was conducted under the supervision of Prof. H. K. D. H. Bhadeshia in the Department of Materials Science and Metallurgy, Cambridge between July 2001 and October 2001. This dissertation contains less than 15,000 words.

Except where acknowledgement and reference is made to previous work, this work is to the best of my knowledge. Neither this, nor any substantially similar dissertation has been, or is been, submitted for any other degree, diploma or qualification at any other university.
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<td>Ni(CO)$_4$</td>
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<td>$\lambda_m$</td>
<td>Mean free path</td>
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<td>$f$</td>
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</table>
\( \lambda \) wavelength

\( SIL \) Sound intensity level

\( SPL \) Sound power level

\( \alpha \) Sound absorption coefficient

\( \rho_0 \) air density

\( \omega \) Angular frequency

\( \omega_i \) undamped frequency

\( X \) amplitude

\( x \) displacement of base

\( y \) deflection of mass

\( m_i \) mass per unit area
OBJECTIVE

Metallic foams have now been researched for many decades. However, the Defence Evaluation and Research Agency is interested in very thin metallic foams containing closed-cell pores. The fraction of porosity in these sheets of foams is at the moment about 0.5 but the intention is to increase the fraction to 0.8 or higher. A number of questions arose during research on these foams:

1) How does the thermal conductivity and noise attenuation vary as a function of porosity for these thin sheets of foams?

2) Is there any pore size dependence of these properties?

A search of the literature revealed considerable work on the modelling of thermal conductivity and noise attenuation but not specifically for the fraction of interest nor anything about pore size dependence. A solution to this problem was the aim of this research.

The research begins with an introduction of the many ways of manufacturing metallic foams containing large fractions of porosity and their applications. Such materials in principle combine good mechanical properties with a reduction in weight.

It then explains the thermal conductivity of metallic foams, and summarizes previous models and their shortcomings. To overcome the shortcomings a new, simple-cube model was created and the thermal conductivity was calculated as a function of porosity. It showed that the thermal conductivities could be estimated for any level of porosity. The size dependency was also investigated using two smaller cubes within the cube model. A sphere model was also developed to see if shape could affect thermal conductivity, but the thermal conductivity could then only be calculated for small fractions due to stereological effects. The effect of gas pressure in the spheres on thermal conductivity was also investigated but it showed that the pressure is independent of thermal conductivity. The work confirmed no effect of pore size on thermal conductivity.
Finally the nature of sound, its properties and different mechanisms of sound attenuation were briefly described. Previous models for measuring sound absorption were summarized and a model was applied to study sound absorption as a function of frequency.
1. METALLIC FOAMS

Metal foams are similar to any other foam (i.e. bath foam, aero chocolate) but recently there has been considerable interest in their properties. Typically about 80-90% of the structure of a modern metallic foam is made of pores, which can be connected together giving an open cell foam or isolated giving closed cell foam made of separate cells which trap gas inside the metal Figure 1. Aluminium foams are important due to their high strength and stiffness for a given weight.

Figure 1(a) Scanning electron micrograph (SEM) of an open-cell aluminium foam from DOUCIEL (b) X-ray tomography of a closed-cell aluminium produced by a continuous process of gas injection to a viscous melt [1].

1.1 CHARACTERISING THE PROPERTIES OF METALLIC FOAMS

High porosity metallic foams are characterised by the morphology of the porous cells (cell geometry, open or closed), cell topology, relative density, cell size, cell shape, properties of the cell wall and the degree of anisotropy.

The mechanical properties of open and closed cell foams differ significantly. The linear elastic response in an open-cell foam is due to the bending of the cell walls. In a closed-cell foam the cell walls stretch and the air or other gas within the cell is compressed.
The expressions for modulus, elastic, plastic and brittle collapse stresses, the fracture toughness and the strain at which densification occurs can be derived by examining the way in which cell edges respond to stresses. This gives a good description of the behaviour of open cell foams. For closed cell foams the deformation of the cell faces as well as the cell edges and the response of the fluid (usually gas) within the cells must be included to give a complete description of the foam [2].

1.2 PRODUCTION OF FOAMS

There are a number of processing routes available for the manufacture of metal foams, including bubbling gas through molten alloys, stirring a foaming agent through the melt, consolidation of metal powders with a particulate foaming agent, and pressure infiltration of the molten metal into a wax or polymer-foam precursor.

Each method can be used to create a porous material with a limited range of relative densities and cell sizes. Each production method has its own structure, densities and imperfections. These imperfections can be variations in cell-walls thickness or non-uniform cell shape. The structures can be characterised using optical microscopy, X-ray tomography, and scanning electron microscopy.

1.2.1 From Melts

Metallic melts can be foamed in one of three ways: by injecting gas into the liquid metal from an external source, by causing in-situ gas formation in the liquid using gas-releasing agents, or by causing the precipitation of gas which was previously dissolved in the liquid.

The simplest method is to bubble air into the bottom of a vat of molten aluminium and cool the bubbles that form at the top [3]. The metal needs fine ceramic particles in it to make it viscous or the air would just escape at the top of the surface without foaming bubbles. This can create closed-cell foams 1 m wide to 0.2 m thick slabs with diameters between 5 and 20 mm. ALCAN in Canada supply foamed aluminium using this process. The relative densities of the foam are between 0.03-0.1. The process is shown in Figure 2.
The Shinko Wire Company in Japan first invented a process, which was based on the mixing of titanium hydride powder into the molten aluminium to generate hydrogen [4]. They developed aluminium foam with the trade name Alporas. This method produced better foams, which have more uniform pore sizes by using a solid foaming agent, which can be mixed into the aluminium before giving off a gas rather than just adding the gas directly. This gives control of the location and size of the pores. The cell size can be varied from 0.5 to 5 mm by changing the TiH₂ content and the foaming and cooling conditions. The relative densities of the foam can vary from 0.2 to as low as 0.07, Figure 3.

Using this process the entire volume is foamed at once, which then gives finer pores and a more regular structure. In the melt gas injection method the viscosity of the molten aluminium has to be increased by mixing powders and fibres but in the gas releasing particle decomposition method, calcium can be added to increase viscosity [4].
An alternative way to form metallic melts is from a casting technique for foam open-cell foams. It is thought that ERG manufactures DUOCELL in this way [5]. A wide range of sizes of great uniformity can be obtained. This method is called infiltration, where some sort of solid mould of pore shapes is made and then molten metal is poured followed by removal of the mould. For example, an open cell polymer template with the desired cell size and relative density is used. This is then coated with a mould casting slurry (ceramic powder), which is then dried and embedded in sand. The mould is then baked to harden the casting material and to decompose the polymer template. Subsequently the mould is filled with a metal alloy and allowed to cool. After cooling the mould materials are removed leaving the metal foam equivalent to the original polymer foam, Figure 4. There are other mould materials, which can be used, for example, plaster or plastics foam. This gives highly uniform open cell foam structures, but the disadvantage is that the procedure is expensive and complicated.

**Figure 4** Investment casting method to manufacture open cell foams (DUOCELL process)[5].
1.2.2 POWDERS

Metal foams can be made from the metal powders (Al and its alloys) and foaming agents (TiH$_2$, ZrH). The metal and foaming agents are blended and cold-compacted. Compaction methods include uniaxial compression, extrusion or powder rolling. The foaming agent is distributed uniformly in the metal matrix, Figure 5 [6].

Extrusion can be used to produce a bar or plate and also helps to break the oxide films at the surfaces of the metal powders, thereby facilitating consolidation. The product is a precursor material not fully dense and after chopping into small pieces, is placed inside a sealed split-mould. This can then get converted into foam by heating at a temperature at which the alloy is partially liquid, with evolving gas converting the assembly into foam. For example, titanium hydride when used as the foaming agent, decomposes creating voids containing hydrogen at high pressure. These expand by semi-solid flow and create foam that fills the mould. The relative densities achieved from this process can be 0.08 and the shape depends on that of the mould. The foam has a closed-cell structure with pore diameters in the range 1-5 mm. This process is called baking, Figure 5 [6].

**Figure 5** *The sequence of powder metallurgy steps to form foams by gas releasing particles in semi-solids* [6].
1.2.3 DEPOSITION

In this process, an open-cell polymer foam is used on to which metals are deposited by chemical vapour deposition (CVD), by evaporation or by electro-deposition. For example, nickel is deposited by the decomposition of nickel carbonyl Ni(CO)\(_4\). The polymer foam is placed in a CVD reactor where nickel carbonyl is introduced. This decomposes into nickel and carbon dioxide when heated to 100°C and coats all the heated surfaces of the polymer foam. After all the metal has been deposited on to the polymer foam, the metal-coated polymer is removed from the CVD reactor and the polymer burnt out by heating in the air, to leave a cellular structure with hollow ligaments. A sintering step can be used to densify the ligaments. The pore size can be varied over a wide range. It is possible to produce pore sizes of 100-300 µm diameter range. The lowest densities available are 0.02-0.05 Figure 6 [7].

**Figure 6** Schematic steps of CVD process used to create open-cell nickel foams [7].

1.3 APPLICATION OF METAL FOAMS

The process described can be used to create porous materials with a range of densities and cell sizes. The structures formed can contain either open or closed-cells. Closed cell foam structures are used mainly for energy absorption applications whilst the open-cell foams are often used for thermal management.

No single property of metallic foam is particularly exceptional - individual material properties of metal foams are available in numerous other materials. Metal foams in general, and aluminium foam in particular, do however, possess a unique combination
of properties not shown by any other material - notably high strength, low density, high melting point, good acoustic absorption, and the ability to absorb large amounts of energy at a low stress when compressed in any direction.

1.3.1 Structural

Foams basically combine relatively high stiffness with a lower density than their parent material. It is important to note that, if only the strength is considered, foams often have a similar or slightly worse performance than solid material of the same weight. The advantage of foams becomes apparent when bending stresses are considered as a function of weight. The mass distribution of cellular structures increases the overall moment of inertia of the material, giving a far higher specific bending stiffness and strength than for the corresponding weight of bulk metal. This makes foams useful as high-strength, low-density load-bearing components in automotive and aerospace applications. This could be in the form of direct load-bearing components, but most use are in bonded composites, where foam is used as a central element encased in an outer metal sheet. Compared with conventional honeycomb materials, these are easier to mass-produce, and have increased resistance to shear due to the isotropic nature of foams [8].

Some of the production methods allow the filling of irregular moulds or shapes with foam - for example to make complex shapes, or to fill beams or pipe structures with foam, to provide increased rigidity without significantly increasing the weight. Compared with solid metal components, structures produced using foam cores have been shown to be significantly lighter, while offering notably increased structural rigidity [8].
Figure 7 Metal foam of high stiffness and low-density ideal for sandwich construction [9].

1.3.2 Heat Exchangers

The corrosion resistance, combined with large surface area and a cell wall material with high thermal conductivity, makes open cell foams ideal for use as heat exchanging materials. Closed cells have a much lower thermal conductivity, which makes them good for thermal shielding [10].

1.3.3 Impact

Another category of applications centres on the energy-absorbing properties of metal foams. When compressed, foams show only a small elastic deformation before the start of plastic collapse. In most foams, this collapse involves extensive plastic deformation of the cell walls in a localised band of failed cells, which gradually propagates throughout the material at a low (and almost constant) stress. Dislocation movement in the metal means that a large amount of energy can be absorbed without the stress exceeding a critical value. Because of the isotropic structure of the foam, uniform deformation and energy absorption is possible for any direction of compression. This opens up applications such as a light, cheap, shock-absorbing material in the front body of cars or trains, to protect the occupants in the event of a collision. Figure 8 shows a good compact absorber for automobile bumpers [11].
Metal foams are thus attractive in terms of the amount of plastic deformation they can undergo per unit mass, since the cell walls are relatively unconstrained. In practice, premature structural failure may prevent this potential from being realised. Foams, which exhibit sufficiently ductile local collapse, can be used as energy absorbing blocks to protect the occupants of cars during impact, as a blast protection material, or as temperature-resistant packaging for materials [11].

![Figure 8](image)

**Figure 8** Good impact absorbers good for automobile bumpers [9].

### 1.3.4 Corrosion-resistant and high-temperature filters

Aluminium has good resistance to oxidation and many forms of chemical attack. Open-cell foams with small pore sizes can thus be used as high-temperature or chemically resistant filter materials. Liquid fuel containers could be part-filled with open-cell foams, so that in the event of breakage, flammable materials would at worst seep out gradually and burn on the surface of a block, rather than spilling over a large area before catching fire.

Metal foams are excellent in arresting flames in environments like long pipes and ventilating enclosures. They are both fire proof and highly permeable. They can also be used in blast protection applications [12].

### 1.3.5 Acoustic Applications

The frequency of resonance depends on the ratio of elastic modulus to density as these can be varied independently, foams can be used to eliminate certain frequencies. The damping capacity of foamed aluminium has been shown to be an order of magnitude higher than that of the bulk metal. Foams have also been used as sound proofing
materials. Within porous structures, sound is attenuated by vibration and friction losses as gas flows between cells during propagation repeated reflections within the cell structure gives rise to long paths were full absorption is possible. The acoustic properties of the metal foams can be used where sound absorption is vital i.e. sides of roads to reduce traffic noise [13].

2. THERMAL CONDUCTIVITY

Thermal conductivity can be considered using a bar with one end of the bar at temperature $T_1$ and the other end at a lower constant temperature $T_2$. Heat is
conducted from the hotter to the colder end at a steady rate as the sides are completely insulated. The heat energy passing through any position is the same within the bar [14], Figure 9.

\[ T_1 \text{heat flow} \quad T_2 \]

**Figure 9** *Heat flow along a uniform insulated bar* [14]

The temperature gradient at any position can be defined as the change of temperature per unit distance along the bar:

\[ T_1 - T_2 / L \]  

(2)

The heat flow along an insulated bar depends on (1) the temperature gradient of the bar, (2) the area of cross section of the bar, (3) material of the bar.

As heat flow is proportional to the temperature gradient and the area of cross section, the equation for heat flow in terms of a constant proportionality \( K \) is called thermal conductivity of the material, is [14]

\[ Q = K A (T_1 - T_2) / L \]  

(2.1)

where \( Q \) is the heat flux (the amount of heat flowing per unit time)

The thermal conductivity \( K \) can also be defined as: The heat flux \( Q \) (the amount of heat flowing across a unit area per unit time), induced by the temperature gradient \( dT/dx \). For one-dimensional heat flow it is defined as:

\[ Q/A = K dT/dx \]  

(2.2)

The units of thermal conductivity are J m\(^{-1}\) s\(^{-1}\) K\(^{-1}\). As J s\(^{-1}\) = Watt (W) so the units can also be W m\(^{-1}\)K\(^{-1}\) [14].

### 2.1 Thermal Resistance

The equation for \( K \) is similar to \( I=V/R \) in electrical conduction where \( I \) is the current, \( R \) is the resistance and \( V \) is the voltage. Heat flow requires a temperature difference whereas electric current requires a potential difference. To calculate heat flow we
use \( Q = KA (T_1 - T_2)/L \). \( Q \) and \( I \) are both flow quantities produced by \((T_1 - T_2)\) and \( V \) respectively. So the quantity \( KA/L \) is the thermal equivalent of \( 1/R \). The thermal resistance of a conductor can be defined by [15]:

\[
R_{TH} = L/KA
\]

(2.3)

where \( L \) conductor length, \( A = \text{Area of cross-section} \), \( K= \text{thermal conductivity} \).

2.1.1 Thermal Conductors In Series

A series circuit is one in which resistors are arranged in a chain, so the current has only one path to take. The current is the same through each resistor. The total resistance of the circuit is found by simply adding up the resistance values of the individual resistors by, [15] Figure 10

Equivalent resistance of resistors in series: \( R = R_1 + R_2 + R_3 \)  

(2.4)

\[\text{Figure 10} \] Equivalent resistances of resistors in series \( R_1 + R_2 + R_3 \), currents \( I \) and voltage \( V \) [15].

When two or more materials are in series contact so heat energy passes through one and then through the next. The energy flux passing through them is the same. Using thermal resistances we can treat thermal conductors in series just as we treat electrical conductors in series. This is the thermal resistance series law, which can be used to determine the effective thermal conductivity in porous materials. (see appendix 2.3.1 for the derivation of thermal conductors in series).

2.1.2 Thermal conductors in parallel

A parallel circuit is a circuit in which the resistors are arranged with their heads connected together, and their tails connected together. The current in a parallel circuit
breaks up, with some flowing along each parallel branch and re-combines when the branches meet again. The voltage across each resistor in parallel is the same [15].

The total resistance of a set of resistors in parallel is found by adding up the reciprocals of the resistance values, and then taking the reciprocal of the total, [15] Figure 11.

Equivalent resistance of resistors in parallel: \( \frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3} \) \hspace{1cm} (2.5)

Figure 11 *Equivalent resistances of resistors in parallel* \( R_1 + R_2 + R_3 \), currents \( I_1 + I_2 + I_3 \) and voltage \( V \) [15].

When two or more materials, are in contact so that, they are parallel to each other. The temperature gradient is identical for all paths of heat flow. Thermal conductors in parallel can be treated just as we treat electrical conductors in parallel (see appendix (2.3.2) for the derivation of thermal conductors in parallel).

### 2.2 Thermal conductivity in Foams

The thermal conductivity of foam can be considered as having four contributions (1) conduction through the solid (2) conduction through gas (3) convection within the cells (4) radiation through the cell walls and across the cell voids. Each contribution is explained in detail below.

#### 2.2.1 Conduction in solid phases

Conduction is the flow of heat through a body in response to a temperature gradient. In a porous material, heat transported by this mechanism is reduced due to the introduction of thermal resistances. Where the cross sectional area of the solid is reduced the heat flow will encounter resistance. Thus the heat transported by
conduction in the solid maybe reduced by decreasing the volume fraction of the solid present. Further reductions can be possible if the cells have tortuous shapes [16].

2.2.2 Conduction in gas phase

Heat transfer in stagnant (non-convecting) gas is usually very slow. However, in low-density thermal insulation materials, where other heat transport mechanisms are suppressed it can be a significant factor.

Many high performance insulation materials are evacuated, and others use the low conductivity of gases to fill pores; although these methods reduce heat flow they are only worthwhile at low temperatures where radiation does not play a significant part [16].

2.2.3 Convection

Convection occurs because of hot fluid rising to displace cold fluid. Convection is produced when any fluid is heated because hot fluid has a lower density than cold fluid, due to thermal expansion. So hot fluid is pushed upwards by the surrounding cold fluid causing convection currents. There are two types of convection currents, which can occur, free and forced convection.

In free-convection, this motion is commonly caused by local density differences (which could rise from temperature differences) resulting in buoyancy forces due to gravity. Forced convection is possible where an external agent induces the motion of the gas [17]. This occurs in metallic foams used as heat exchanger but not in insulating foam. Skochdopole [18] determined the effect of free convection in polymer foams by experimental investigations that measured heat transport through the foam as a function of cell size, initially with foam heated on the upper surface and then on the underside. The measured conductivity of top and bottom heating was found to converge for cells below 4mm diameter, so convection was negligible in foams with size cells below 4mm [18].

2.2.4 Radiation
Heat is also transferred by electromagnetic radiation. Stefan’s Law describes the heat flux passing by radiation from one surface to one at lower temperature with vacuum in between them, [19].

\[ Q = \sigma_{sb} T^4 \]  

(2.6)

Where \( \sigma_{sb} \) is Stefan’s constant and \( T \) is the temperature difference.

### 2.2.5 Combination of mechanisms

The overall conduction can be determined by combining the thermal transport mechanisms by simple addition,

\[ K' = K_s + K_g + K_c + K_r \]  

(2.7)

where \( K_s \) is the contribution of thermal conductivity from conduction through the solid, \( K_g \) is that from the gas, \( K_c \) is the thermal conductivity due to convective processes and \( K_r \) is the contribution from radiation [20].

The total thermal conductivity changes with density. For closed-cell foams at minimum relative density of 0.03 and 0.07 the conductivity is little larger than air contained in the cells. The way to reduce it further is by replacing air with a gas of lower thermal conductivity such as trichlorofluoromethane CCl3F. The heat transfer through the cells happens with half through the gas and half through the solid and radiation [20].

Heat transfer increases with cell size. This is because radiation is reflected less often in foam with large cells and partly because for cells more than 10 mm or so in diameter then cell starts to convect [20].

Other factors like the fraction of open cells, affect heat transfer too but to a lesser extent. Temperature is another factor, which can affect thermal conductivity. Thermal conductivity through solids and gases decrease, as the temperature decreases.
Radiation also becomes less effective at low temperatures. Thus the heat transfer in foams decreases steeply with decreasing temperature [20].

### 2.3 Previous Models of Thermal Conductivity

#### 2.3.1 Calmidi and Mahajan Model

Calmidi and Mahajan investigated the effective thermal conductivity $K_e$ of high porosity fibrous metal foams experimentally and derived an empirical correlation [21].

The experiment used an open cell structure with dodecahedron-like cells, which had 12-14 pentagonal or hexagonal faces. The edges of the cells were composed of fibers. The matrix was aluminum alloy T-6201, which had a thermal conductivity of $218 \text{ W m}^{-1} \text{K}^{-1}$. The metal foam was brazed with two aluminum plates. Thermocouples were attached at different distances. The surfaces were insulated by using Styrofoam. The bottom was cooled using a tank with cool flowing water. The direction of heat flow was from the top to the bottom and all the sides were insulated so the heat flowed in one direction [21].

If $Q$ was the net heat flux through the top,

$$Q = K_e A_m \Delta T / L_m$$  \hspace{1cm} (2.8)

where $K_e$ is the effective thermal conductivity, $A_m$ was the area of cross section of the foam and $L_m$ was the height of the foam. The experiments involved using air and water as the fluid phases. There were a few sources of error in the measurements of the thermal conductivity mainly due to the heat loss in thermocouples and the insulating Styrofoam [21].

Based on the experimental data, an empirical correlation was developed, [21].

$$K_e / K_f = K_s (1-\varepsilon)^n A / K_f + \varepsilon$$  \hspace{1cm} (2.9)

where $\varepsilon$ is the porosity and $K_s$ and $K_f$ are the thermal conductivities of the solids and fluid respectively. The best fit was when $n = 0.793$ with the value of $A$ being 0.181
for air and 0.195 for water. The maximum errors were found to be 6.9 and 7.5 percent respectively.

In order to develop a theory, Calamidi and Mahajan assumed two-dimensional foam consisting of an array of hexagons, Figure 12 [21]. The hexagons were intended to represent the metal ‘shell’ of the foam and the nodes within the hexagonal network were represented as squares. In this honeycomb shape, the thickness and length of the ligaments joining the nodes and the length of the edge of the square node was adjustable. As the structure was periodic, a unit cell could be defined on which the analysis could be focused. Heat flow was assumed to be one direction-dimensional.

**Figure 12** *The hexagonal structure of the metal foam matrix* [21].

To achieve effective thermal conductivity $K$, they needed to:

1. Identify the unit cell in the structure, the repetition of which generates within the whole foam.
2. Divide each unit cell into convenient layers 1, 2 and 3, Figure 13.
(3) Needed to calculate the thermal conductivity of each layer 1, 2 and 3 in the unit cell, using the parallel law of thermal resistance which correspond to $K_{L1}$, $K_{L2}$ and $K_{L3}$. (see appendix 2.3.1 for derivation for thermal conductors in parallel), giving:

$$K_{Lj} = K_1 V_1 + K_2 V_2$$  \hspace{1cm} (2.10)

where $K_1$ and $K_2$ were thermal conductivities and $V_1$ and $V_2$ were the volume fraction of materials 1 and 2 (i.e. solid and fluid) respectively.

(4) Needed to sum the conductivities in each of the layers using series law of thermal resistance, (see appendix 2.3.2 for derivation for thermal conductors in series) giving:

$$K_e = \frac{(L_1 + L_2)}{L_1/ K_{L1} + L_2/ K_{L2}}$$  \hspace{1cm} (2.11)

where $L_1$ and $L_2$ are the lengths of materials 1 and 2 (i.e. solid and fluid).

2.3.2 Tetrakiadechedron Model

The Calamidi and Mahajan model of calculating the effective thermal conductivity is simple but very powerful and has been shown to give good results. To make the method more sophisticated Boomsma and Poulakakos determined the thermal conductivity in a three-dimensional foam structure assuming a tetrakiadechedron shape, Figure 14.
**Figure 14** The tetrakaidecahedron modelled by cubical nodes and cylindrical ligaments with the unit cell as a solid block [22].

This model consisted of cubical nodes and cylindrical ligaments. The labelled cubical nodes (1-4) in Figure 14 are represented in Figure 15. The length of each cubical node was $r$ while the length $L$ defined the cylindrical ligament of radius $a$, Figure 15.

![Diagram of tetrakaidecahedron model](image)

**Figure 15** (a) The components of the foam network of the tetrakaidecahedron represented geometrically by cubical nodes and cylindrical ligaments (b) This shows the unit cell of the tetrakaidecahedron [22].

The unit cell given in Figure 15 was divided into convenient layers $L_A$, $L_B$, $L_C$ and $L_D$ of lengths $a$, $r/2 – a$, $0.707L – r$ and $r/2$ respectively. From the lengths of $L_A$, $L_B$, $L_C$ and $L_D$ the total volume of each section $V_A$, $V_B$, $V_C$ and $V_D$ was calculated by multiplying with the unit cells area ($2L^2$) giving
\[ V_A = 2aL^2 \]
\[ V_C = 2(1/2L\sqrt{2} - r) L^2 \]
\[ V_B = (r - 2a) L^2 \]
\[ V_D = r L^2 \]

Then the volume occupied by the solid for each layer was calculated giving:

\[ V_{AS} = ar^2 \]
\[ V_{BS} = r^3/2 - ar^2 \]
\[ V_{CS} = L\sqrt{2/2\pi a^2} - r\pi a^2 \]
\[ V_{DS} = r^3/4 \]

From the volume fractions of each section, the effective thermal conductivity could be calculated for each layer using the parallel law of thermal conductors giving [15]

\[ K_A = (K_1 V_{AS} + K_2 (V_A - V_{AS}))/V_A \]  \hspace{1cm} (2.12)

where \( K_1 \) and \( K_2 \) are the thermal conductivities for two different materials in this case, its Aluminium (\( K_1 = 218 \text{ W m}^{-1}\text{K}^{-1} \)) used as the solid and air is used as the fluid (\( K_2 = 0.0265 \text{ W m}^{-1}\text{K}^{-1} \)).

The total thermal conductivity for the representative section can be calculated from the law of thermal conductors in series, giving [15]

\[ K_{eff} = L_A + L_B + L_C + L_D/(L_A/K_A + L_B/K_B + L_C/K_C + L_D/K_D) \]  \hspace{1cm} (2.13)
3. MODEL DEVELOPMENTS FOR THERMAL CONDUCTIVITY

The tetrakaiadekahedron model was not a very good model as it could only calculate the thermal conductivity for high porosity media (porosities greater than 0.9), and it had no facility for the pore size dependency. There was also a geometrical limit to the lengths of the ligaments at $r = 0.35$ after which the results become invalid. Apart from this it had a complicated structure.

3.1 The Cube Models

Due to the downfalls of the tetrakaiadekahedron model, it was decided to create a new model assuming a cuboidal pore in a cube. The method used was similar to the tetrakaiadekahedron model but with a cube was instead of the tetrakaiadekahedron, Figure 16.

![Figure 16](nanx-7792853509743503177052285428765294592)

Figure 16 The cube model containing a smaller cube representing a pore size with edge $R$.

Initially a large cube was used with dimensions $1 \times 1 \times 1$ metre as shown in Figure 16. The large cube of unit dimensions contained a smaller cube of length $R$ to represent the pore. The large cube was then defined in three layers $A$, $B$ and $C$ of heights as $LA$, $LB$ and $LC$ respectively. It is easy to show that $LA$, $LB$ and $LC$ are $1-R/2$, $R$ and $1-R/2$ respectively. The volume of each section was $V_A$, $V_B$ and $V_C$ was given by $1-R/2$, $R$ and $1-R/2$ respectively. The corresponding volume fractions, $V_{AS}$, $V_{BS}$, and $V_{CS}$ were therefore $1-R/2$, $R - R^3$ and $1-R/2$ respectively.

Similar to previous models, the thermal conductivity ($K_A$, $K_B$, $K_C$) of each layer ($A$, $B$ and $C$) respectively could be calculated using the law of parallel thermal conductors
\[ K_A = (K_1 V_{AS} + K_2 (V_A - V_{AS}))/V_A \]  

(3.1)

where \( K_1 \) and \( K_2 \) are the thermal conductivities for two different materials in this case was Aluminium (\( K_1 = 218 \text{ W m}^{-1} \text{ K}^{-1} \)) used as the solid and air is used as the fluid (\( K_2 = 0.0265 \text{ W m}^{-1} \text{ K}^{-1} \))[21].

The effective thermal conductivity was obtained from the law of series thermal conductors [21]

\[ K_{\text{eff}} = L_A + L_B + L_C/(L_A/K_A + L_B/K_B + L_C/K_C) \]

(3.2)

In order to determine whether the pore size has an effect on thermal conductivity, the single cuboidal pore was replaced with two smaller cubes with the same total volume as the single cube. Each of the smaller cubes had an edge length 0.7937R where R is the edge length of the single cube pore, (0.7937 is derived by dividing the volume of the larger cube R by 2 as there were two equivalent volumes of smaller cubes and then calculating the edge length).

Figure 17 The cube model containing two smaller cubes representing pore sizes with edge 0.7937R

2.3.2 The Sphere Model

An alternative approach was using a sphere in a cube model. This was to determine if the shape of pore has any effect on thermal conductivity, and also wanted to determine what effect gas pressure would have on thermal conductivity. The
corresponding volume fractions of solid are \( \frac{4}{3} \pi R^3 \), Figure 14. The cube was then defined in three sections \( A, B \) and \( C \). The height of each section was calculated, as section \( LA=1-2R/2, \, LB=2R \) and \( LC=1-2R/2 \). The volume of each section was therefore \( V_A=1-2R/2, \, V_B=2R \) and \( V_C=1-2R/2 \) and the corresponding volume fractions of solid are \( 1-2R/2, \, 2R-4/3 \pi R^3 \) and \( 1-2R/2 \) respectively.

Similar to previous models, the thermal conductivity of each layer \( (K_A, K_B, K_C) \) was calculated using the law of thermal conductors in parallel giving (see appendix 2.3.1 for derivation)

\[
K_A = (K \, V_{AS} + K_2 (V_A - V_{AS}))/V_A
\]

(3.1)

where \( K_1 \) and \( K_2 \) are the thermal conductivities for two different materials in this case its Aluminium \( (K_1=218 \text{ Wm}^{-1}\text{K}^{-1}) \) used as the solid and air is used as the fluid \( (K_2=0.0265 \text{ Wm}^{-1}\text{K}^{-1}) \).

The effective thermal conductivity \( (K_{eff}) \) was obtained from the law of thermal conductor in series (see appendix 2.3.1 for derivation)

\[
K_{eff} = L_A + L_B + L_C/(L_A/K_A + L_B/K_B + L_C/K_C)
\]

(3.2)

**Figure 18** The sphere model of a unit cube sphere of diameter 2R inside.
4. RESULTS AND DISCUSSION.

FORTRAN programs were written for the thermal conductivity of the tetrakaidecahedron, cube models and sphere models (see appendix for details of the FORTRAN programs tetramodel.f, cube1.f, cube2.f, sphere1.f and sphere2.f).

The tetrakaidecahedron model was not a very good model as it could only calculate the thermal conductivity for high porosity media (porosities greater than 0.9), and it had no facility for the pore size dependency.Apart from this it also has a complicated structure. There was a geometrical limit to the length of the ligaments at \( r > 0.35 \) after which the results became invalid.

Due to the downfalls of the tetrakiadecahedron model, a simple 3-dimensional cube model was developed and the thermal conductivity was calculated. The theory behind the model was similar to the tetrakaidecahedron model but with a cube as the unit cell.

By varying the edge length \( R \) of the cuboidal pore, the thermal conductivity could be measured for all values of porosity. The values of thermal conductivity thus obtained were plotted as a function of porosity. Similarly for the cube with two smaller cubes (cube 2) the values of thermal conductivity obtained were plotted as a function of porosity, Figure 19.

![Figure 19](image)

**Figure 19** Thermal conductivity of the cube 1 and cube 2 where cube 1 is the cube model with one small cube and cube 2 is the cube with two smaller cubes as a function of porosity

The two plots didn’t show any important differences indicating that the effect of pore size at low porosities has no significant effect on thermal conductivity but for cube 2
there was a limit when \( R = 0.8 \) (porosity = 0.61) at which both the pores start to overlap and a invalid value is obtained, Figure 19.

However, when the tetrakiadechaedron model and cube models were compared, it was found that the tetrakiadechaedron model offers no advantage over the simple cube model, Figure 20. Therefore, the cube models could be used instead of the tetrakiadechaedron model and the thermal conductivity could be calculated for all porosities.

![Comparison of the thermal conductivity of the tetrakiadechaedron and cube model as a function of porosity](image)

**Figure 20** *Comparison of the thermal conductivity of the tetrakiadechaedron and cube model as a function of porosity*

From the sphere model it was intended to determine how shape could affect thermal conductivity. The sphere model showed, it also had a limit for which the thermal conductivity could be calculated and that was when \( R = 0.5 \), otherwise the values become invalid because then the sphere then exceeds the bounds of the cube.

The effect of pore size dependency was also considered using two small spheres of radius \( R \) (sphere 2) and the thermal conductivity was measured. It showed that when \( R > 0.43 \) the spheres start to overlap.
Figure 21  *Thermal conductivity of the sphere 1 and sphere 2 where sphere 1 is the sphere model with one small sphere and sphere 2 is the sphere with two smaller spheres as a function of porosity*

The cube and sphere models were also compared and showed that the effect of shape does not have much effect on the thermal conductivity. The limits for the sphere cube are much less as compared to the cube model. So cube model is the best option to measure thermal conductivity.

Figure 22 *Comparison of the thermal conductivity of the sphere 1 and cube 1 model as a function of porosity*
Now from the sphere model we could also determine what effect gas would have when put in the spheres.

Initially, this can be determined by focusing on the influence of the effect of pressure with pore size. The pressure of the sphere depends on the pressure \( P \) inside the sphere and the pressure outside the sphere, which is the surface energy \( \gamma \) and can be given by

\[
\pi R^2 P = 2\pi R \gamma \tag{4.1}
\]

\[
P = 2\gamma R \tag{4.2}
\]

where \( R \) is the radius of the sphere. The above equation shows that pressure is inversely proportional to the pore size. Thus, the smaller the sphere the higher the pressure.

From [23] it showed that thermal conductivity was independent of pressure. The thermal conductivity of a perfect gas is given

\[
K = \frac{1}{3} \lambda c C_{V,m} [A] \tag{4.3}
\]

where \( C_V, m \) is the molar heat capacity at constant volume, the molar concentration \([A]\) and \( \lambda \) is the mean free path.

Because each molecule carries an average energy because \( \lambda \) is inversely proportional to the pressure and hence inversely proportional to the molar concentration of the gas, it shows that thermal conductivity is independent of pressure. The physical reason for this independence is that thermal conductivity can be expected to be large when many molecules are allowed to transport the energy but the presence of so many molecules limits their mean free path. So the energy cannot carry the energy over a great distance, and thus the effects balance [23]. Therefore, this effect confirms that sphere pore size has no effect on thermal conductivity.