A New Group Contribution Method for the Estimation of Thermal Conductivity of Non-Electrolyte Organic Compounds

By

Onellan Govender [B.Sc. (Eng.)]

University of KwaZulu-Natal Durban
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Examiner’s Copy
Abstract

The optimum design of heat and mass transfer equipment forms an integral part of cost-effective plant design. For this purpose, reasonably accurate thermal conductivity data are required for all phases. Modern reliable equipment is now available for the routine measurement of liquid thermal conductivity but due to the large amount of data needed and costs of experiments, alternative sources such as predictive methods are often employed. Substantial effort has been invested into the development of models for prediction and correlation of liquid thermal conductivity. Prediction of liquid thermal conductivity based solely on a theoretical basis does not provide reliable results as the theories used to describe the liquid state are seldom satisfactory (Rodenbush et al., 1999). Therefore, prediction of thermo-physical properties is most often based upon empirical approaches like group contribution methods.

Methods for the estimation of the normal boiling point (Cordes and Rarey, 2002, Nannoolal et al., 2004), critical property data (Nannoolal et al., 2007), vapour pressures (Moller et al., 2008, Nannoolal et al., 2008) and liquid viscosity (Nannoolal et al., 2009) have previously been developed in our group using the group contribution approach. Based on these methods a more accurate and precise method with a better temperature dependency is presented for liquid thermal conductivity prediction. The data used to develop the method was obtained from the extensive Dortmund Data Bank (DDB) (Gmehling et al., 2009), which contains approximately 110000 pure component thermal conductivity data points for almost 900 different compounds for the various phases. Only a third of the components and even fewer data points were usable after critical evaluation; however, the model still has a wider range of applicability than previous correlations and models, which were based on smaller experimental data sets.

The relative mean deviation (RMD) for the training set was found to be 3.87 % (331 compounds and 6264 data points). Applicability to data outside the training and performance of the model was tested using an external set of liquid thermal conductivity data. The RMD for the test set was 7.68 % for 38 compounds (328 data points). This error was found to be high as the test set contained data extrapolated from experimental data at elevated pressures, and other less reliable data which was excluded from the training set. The results from the test set show that the method may be applied to components outside the training set with reasonable confidence.
Preface

The work presented in this dissertation was undertaken at the University of KwaZulu-Natal Durban from February 2009 until November 2011 and was supervised by Professor Dr. D. Ramjugernath and Professor Dr. J. Rarey.

I **Onellan Govender** declare that:

(i) The research reported in this dissertation/thesis, except where otherwise indicated, is my original work.

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As the candidate’s Supervisor I agree/do not agree to the submission of this thesis.

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Prof. Dr. D. Ramjugernath
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Nomenclature

a, b, c, d, e - model parameters/constants
A, B, C, D, E - model parameters/constants
M - molar mass (g.mol⁻¹)
n - number of moles
P - pressure (kPa)
R - ideal gas constant (J.mol⁻¹.K⁻¹)
S - entropy (J.mol⁻¹.K⁻¹)
T - absolute temperature (K)
V - molar volume (cm³.mol⁻¹)
Z - compressibility factor

Greek symbols
λ - thermal conductivity (W.m⁻¹.K⁻¹)
μ - chemical potential
w - Pitzer acentric factor

Subscripts
b - normal boiling point
c - critical point
n - molar basis
r - reduced property
vap - vaporization

Superscripts
s - saturated / solid
l - liquid
v - vapour

All other symbols used are explained in the text and unless otherwise stated SI units have been used.
1. Introduction

The design of unit operations in industry is based upon the modelling of mass, momentum or heat transfer for the different processes. This requires fairly accurate transport property data for the evaluation of transfer coefficients and dimensionless numbers which are involved in the design of equipment such as plug flow reactors, heat exchangers, flow meters, distillation columns, pumps, etc (Nieto de Castro, 1990, Rodenbush et al., 1999). Optimum design of heat and mass transfer equipment forms an integral part of cost-effective plant design.

In a study undertaken by Fujioka et al. for the design of a chemical heat pump to be used with a solid catalyst bed reactor (Fujioka et al., 2006), a problem was encountered where a strongly exothermic reaction formed products with low thermal conductivities. This prevented heat from being effectively removed from the reaction. Research performed by the group indicated that an increase of the effective heat transfer coefficient, up to a limit, could be used to decrease the reaction time down to a minimum. Thus, design of the equipment could not be carried out without prior simulation of the equipment to determine whether operation under the specific conditions was viable. In this design, the reaction rate was controlled by process heat transfer; thus accurate transport data, thermal conductivity in particular for heat transfer calculations, was required. The thermal conductivity for the reactants, products, catalysts and reaction vessel can therefore play an important role in reactor design.

During the experimental determination of thermal conductivity of fluid phases, convective heat transport has to be strictly avoided. Although modern reliable equipment is now available for the routine measurement of liquid thermal conductivity, due to the large amount of data needed and the costs of experiments, alternative sources such as predictive methods are often employed. Many simulation packages such as ASPEN® or HYSYS® use built in predictive methods to provide physical, thermodynamic, and transport properties during process modelling and simulation.

There are many methods available for the prediction of thermal conductivity. However, many are either complex or require the input of numerous other properties (Horvath, 1992). Routine prediction of transport properties in an engineering context requires a method which is fast, simple to implement and has minimum input requirements. Complex equations or the input requirement of a number of properties may introduce errors into the calculation, which can then be difficult to trace when introduced into a process simulation. To satisfy the aforementioned need, researchers have correlated data using equations which require only inputs of either molecular mass, normal boiling point, or correlated constants, together with the temperature for which to calculate or estimate the thermal conductivity (Horvath, 1992, Lakshmi and Prasad, 1992, Poling et al., 2004).

It is for the above reasons that the group contribution concept has become increasingly popular for the prediction of thermodynamic, thermophysical and transport properties. It is based on the principle that the properties of a pure component can be predicted using only the structure of the molecule and the state variables. In the group contribution method, the property of a pure compound is calculated from
the sum of the contributions of the structural groups (e.g. -CH₂, -CHOOH, -C=C- etc.) of which it is composed. The basic group contribution principle is based on the assumption that the effects of the individual structural groups are additive (Moller, 2007). This additivity does not need to be with respect to the property itself but may be for a general function of the property. This function usually contains several empirical model parameters.

Seven group contribution methods and numerous empirical and semi-empirical correlations for liquid thermal conductivity prediction have been found in literature. These methods provide a limited temperature dependency and limited range of applicability. Prediction of liquid thermal conductivity from molecular and kinetic theory often leads to unsatisfactory results as the theories used to describe the liquid state are often insufficient (Rodenbush et al., 1999) to describe the energy transfer due to collisions within the fluid.

Intermolecular forces govern the liquid behavior, and in some aspects, liquids more closely resemble a solid than a gas. Therefore, utilising kinetic theory may work extremely well for the vapour phase, but not for liquids.

Work done to date on group contribution method’s by the UKZN Thermodynamics Research Unit in collaboration with the Carl von Ossietzky University includes the estimation of the normal boiling point (Cordes and Rarey, 2002, Nannoolal et al., 2004), critical property data (Nannoolal et al., 2007), vapour pressures (Moller et al., 2008, Nannoolal et al., 2008) and liquid viscosity (Nannoolal et al., 2009).

This study aims to improve upon available thermal conductivity prediction methods with respect to the range of applicability, temperature range within which the method is applicable, accuracy and precision of prediction by implementation of the group contribution concept to a much larger collection of thermal conductivity data than previously available. The tasks which were required for the fulfilment of the aim are:

i. Undertaking a comprehensive review of all relevant literature;

ii. The compilation and critical evaluation of all the necessary experimental data to yield a suitable data set (training set) which will be used for the regression of the structural contributions;

iii. Development of a new empirical or semi-empirical model which would describe the experimental data more accurately;

iv. Regression of the model parameters using the training set;

v. Regression of structural contributions based upon model parameters;

vi. Testing of the model using an independent set of experimental data (test set).
2. Theory and Literature Review

2.1. Introduction

It is well known that temperature gradients are the driving force for heat transfer either within or between phases. Energy in the form of heat is always transferred from a region of high temperature to one of low temperature. Conductive heat transfer occurs within a single phase (e.g. heat transfer through a pipe wall) irrespective of the phase (gas, solid or liquid). Conductive heat transfer is given mathematically by Fourier’s law as follows:

\[ q = -\lambda \nabla T \]

In the above equation, \( \lambda \) is the thermal conductivity or transfer coefficient which relates \( q \), the heat flux and \( \nabla T \), the temperature gradient (Assael et al., 1998). Thermal conductivity is therefore the ability of a material to conduct heat or the degree to which the material can conduct heat. Assuming that heat transfer occurs in one direction only and that the material is homogeneous (\( \lambda \) constant with respect to \( x \)), Eqn. (2.1) may then be integrated producing the following analogous equation for one-dimensional heat conduction:

\[ \dot{q} \Delta x = \lambda \Delta T \]

where \( \Delta x \) is the shortest distance between two parallel layers inside the homogeneous phase and \( \Delta T \) is the temperature difference between these layers. If the temperature difference is constant with respect to time then the heat flux is constant with respect to time and the following holds:

\[ \dot{\lambda} = \frac{\Delta Q \Delta x}{\Delta t \Delta A \Delta T} \]

where \( \Delta Q \) is the amount of heat transferred in the time interval \( \Delta t \) through an area with cross section \( A \). In this equation, \( \lambda \) is a material constant that depends on temperature and pressure (density) and the kind of material (pure component or mixture). Thermal conductivity may thus be described as the rate at which heat transfer occurs within a system in a state of non-equilibrium (Assael et al., 1998).

2.2. State Variable Dependency

Any transport property, for example, thermal conductivity, may be written in terms of the state variables temperature and density (density has a more linear relationship with thermal conductivity than pressure as will be shown later on) as a function of three contributions as follows (Assael et al., 1998):
\[ \lambda(\rho_n, T) = \lambda_o(T) + \Delta\lambda(\rho_n, T) + \Delta\lambda_c(\rho_n, T) \]  \hfill (2.4)

The three contributions of Eqn. (2.4) represent the dilute-gas contribution (i.e. negligible pressure effect), the excess contribution (pressure effect) and the critical enhancement contribution (Assael et al., 1998). The sum of the first two contributions (dilute-gas and excess contribution) is called the background contribution of the transport property. The background contribution represents the thermal conductivity of the liquid sufficiently below the critical temperature and is the term most often predicted for transport properties.

The background term, according to Ely and Hanley (Ely and Hanley, 1983), may be divided into two different contributions as compared to those stated above. The first due to the transfer of energy from solely collisional or translational effects, and the second resulting from the transfer of energy via the internal degrees of freedom.

The divergence of transport properties at the critical point is known as “critical enhancement”. This critical enhancement contribution may be described as the difference between the actual property at the critical point and the extrapolated value of the property from lower temperatures or pressures.

When approaching the critical point, the mean free path of the molecules is in the order of the mean distance between the particles and the differential \[ \frac{\partial P}{\partial V} \] approaches zero. In this way the stabilizing effect of the pressure that usually provides homogeneity in density (or molar volume \( V \)) is lost and strong fluctuations lead to strong increase of all transport phenomena. As shown in Figure 2.1, liquid thermal conductivity shows strong enhancement around the critical region.

![Figure 2.1: Thermal conductivity vs. density for methane around the critical region (\( T_c = 190.6 \text{ K} \))](image)

(Mathias et al., 2002)
A review of available experimental data has indicated that there are large amounts of data measured at high pressures (reduced pressures in the order of 5.5 to 200). There are however very few methods available in literature which account for the pressure dependency.

![Figure 2.2: Thermal conductivity vs. temperature for cyclopentane at 1atm (data from the DDB (Gmehling et al., 2009))](image)

For most organic liquids thermal conductivity has an inversely linear relationship with the state property temperature at low pressures as shown in Figure 2.2. This relationship has been used many times for the correlation of organic liquid thermal conductivity data (Horvath, 1992, Lakshmi and Prasad, 1992, Nagvekar and Daubert, 1987, Reidel, 1951, Sastri and Rao, 1993, Sastri and Rao, 1999).
As the pressure is increased, the linear trend followed starts to curve into a slightly parabolic trend. As seen for propane in Figure 2.3 above, this tends to occur at moderately high pressures of 100 to 500 bar and upwards. However, the temperature trend is normally not described at higher pressures. Rather, the pressure or density dependency is described at a set temperature as this would eliminate the requirement of representing a complicated thermal conductivity model.

Except for the region in which critical enhancement occurs, liquid thermal conductivity has a weak dependency upon pressure. The dependency follows a fairly linear trend up to moderately high pressures, as may be seen from the deviation of the data to the parabolic trend line in Figure 2.4 below. However, at higher pressures, it can be clearly seen that a very weak parabolic trend is followed, thus indicating the requirement of a high change in pressure to obtain a small change in liquid thermal conductivity.

Figure 2.3: Thermal conductivity of propane as f(T,P) (Rarey, 2009)
Figure 2.4: Thermal conductivity vs. pressure for 1-octene at 320K (data from DDB (Gmehling et al., 2009))

When compared to the trend followed by pressure, the dependence upon density is much simpler. It is due to this simple linear trend that density is widely used for modelling of the pressure dependence. The problem with using density as a dependent variable is that pressure is the much more common and easier variable to measure. And since density is dependent upon temperature and pressure, accurate methods are required to convert from the experimental pressure and temperature to a usable density.

Figure 2.5: Liquid thermal conductivity vs. density for 1-octene at 320K (♦ - exp. data from DDB (Gmehling et al., 2009))

Liquid thermal conductivity does not follow a linear trend for all organic compounds such as that of 1-octene as in Figure 2.5 above. Compounds containing multiple hydrogen bonds deviate from the
standard behaviour as shown in Figure 2.6 below. This deviation from the linear trend of straight chained hydrocarbons may be ascribed to the interaction between multiple hydrogen bonds and is explained later on.

![Figure 2.6: Liquid thermal conductivity vs. temperature for tetra-ethylene-glycol (exp. data from DDB (Gmehling et al., 2009))](image)

2.3. **Experimental Methods**

There are two primary types of equipment used for the experimental determination of thermal conductivity:

(A) Those employing cylindrical surfaces; and

(B) Those employing plane parallel surfaces.

From the above two types of equipment, there are three methods which have given the most reliable results. These three are the flat plate method (employs equipment of type B), the filament method (employs equipment of type A), and the concentric cylinder method (employs equipment of type A).

In the filament or hot wire method, the inner surface is a fine wire supplied with heat by passing a current through it and measuring its temperature by measuring its resistance. A single, non-compensating tube is normally used which contains the coiled hot-wire filament. This equipment has to be calibrated against known standards to account for end effects. Data for a compound for which accurate and precise data are available is used for calibration. A correction to the above method is the use of two tubes of different lengths in order to calculate corrections due to the end losses.
A modification of the above method is the concentric cylinder method. The test liquid is contained in the annulus between two concentric cylinders and heat is supplied along the axis of the inner cylinder. The temperature difference across the liquid layer in the inner tube is then measured. The main problems with this method are getting the two cylinders to sit concentric and the measurement of the thickness of the annulus.

In the flat plate method, liquid is contained between two horizontal plates. The heat is supplied to the top plate, and the temperature drop across the liquid film between the two plates is then measured. Precautions have to be taken to reduce heat loss as the heat is supplied external to the liquid layer. Evaporation of the test liquid along the edges of the plates may result in higher temperature gradients making this method unreliable for volatile liquids and creating a greater discrepancy in results.

These are the basic types of experimental equipment which are used in a laboratory. Experimental equipment used by industry may be much more sophisticated, eliminating convection almost completely such as the Transient Plane Source (TPS) (ThermTest-Inc, 2010) or more generalised equipment such as the DRX-I-YTX Fluid Liquid Material Thermal Conductivity Testing Equipment (2010). However, most of these results are usually not published.

### 2.4. Data Correlation Models

When developing a method for prediction of a thermophysical property the first step is to select an equation, which can fit the experimental data sufficiently well without employing an excessive number of variables or input parameters. Millat et al. (Millat et al., 2005) suggested that for a direct fit to thermal conductivity data the following relationship is sufficient:

\[
\lambda = A + BT + CT^2
\]  

(2.5)

where A, B and C are model parameters. Since thermal conductivity is a function of both temperature and pressure this equation is only applicable to isobaric data or data along the vapour-liquid saturation line.
Figure 2.7: Liquid thermal conductivity vs. temperature for bromobenzene utilizing a linear trend for correlation of data ( ■ – experimental data from DDB (Gmehling et al., 2009))

Figure 2.8: Liquid thermal conductivity vs. temperature for bromobenzene utilizing a polynomial fit for correlation of data ( ■ – experimental data from DDB (Gmehling et al., 2009))

However, thermal conductivity depends almost linearly on temperature resulting in a small value of \( C \) for Eqn. (2.5) above. As shown in Figure 2.7 and Figure 2.8 above, changing from a linear fitted model to a second order polynomial allows the predictor variable (temperature) to explain an increase of only 1.1% in the variance of the experimental liquid thermal conductivity data. For the accurate representation of pure component thermal conductivity, equations, which contain both temperature and pressure dependence are used (Nemzer et al., 1996).

Jamieson (Jamieson, 1979) found the simplest equation suitable to represent thermal conductivity data for all organic liquids as:

\[
\lambda = A(1 + B \tau^{1/3} + C \tau^{2/3} + D\tau)
\]

(2.6)
The above equation (similar to that of Wagner (Wagner, 1977) for vapour pressure) takes into account the chemical structure through the parameter ‘A’, which is be called the pseudo-critical thermal conductivity, ‘B, C and D’ are parameters which are correlated for different components and \( \tau = 1 - T/T_c \). The above equation was modified by Jamieson to consist of two parameters which are correlated to the chemical structure of different compounds. However, the resulting equation, Eqn. (2.7) below, may only be used with alkanes, alkenes, dienes, aromatic hydrocarbons, cycloalkanes, aliphatic and aromatic esters and ethers, and halogenated aliphatic and aromatic hydrocarbons.

\[
\hat{\lambda} = A(1 + B\tau^{2/3} + [1 - 3B]\tau^{2/3} + 3B\tau) \tag{2.7}
\]

However, Eqns. (2.5) to (2.7) are not applicable to glycols or liquids displaying behaviour similar to that of Figure 2.6.

2.5. Predictive Models

The previous section introduced ways for representing the behaviour of thermal conductivity data. However, experimental data may not always be available for this task. It is therefore desirable to have predictive methods, which could be used for property prediction when experimental data are unavailable. Some of the popular prediction methods are outlined below. Predictive methods may be split into five main categories:

- **General correlation methods** – these methods are typically based on one or more pure component properties. Typical properties used in these methods are molar mass, liquid density, heat capacity at constant pressure, heat of vaporization, or the normal boiling point. As these methods will not be considered in the development of the new model, they shall not be given a full critical review. An excellent review of a large number of correlation equations has been compiled by Horvath (Horvath, 1992). The book covers all methods for thermal conductivity predictions from the initial study by Weber in 1880, up to those by Herrick and Lielmezs, and Kerr in 1985.

- **Family methods** – in these methods, equations are regressed to data according to the chemical family into which they fall. The applicability of the methods depends on the definition of the chemical family. An example of this is the method by Latini et al. (Poling et al., 2004). Usage of these methods is limited to the chemical families for which the models were developed. This type of method comes closest to the idea behind the group contribution scheme.

- **Group contribution methods** – As mentioned, these methods are similar to the family methods, but are much more widely applicable if the structural groups are well defined for the property. The application of these methods includes the regression of the group values against available data and then using these groups to predict thermophysical properties (in this case thermal conductivity) of any compounds for which structural groups are available.
- Corresponding states methods – The theory of corresponding states, states that “all fluids, when compared at the same reduced temperature and reduced pressure, have approximately the same compressibility factor and all deviate from ideal gas behaviour to about the same degree” (Smith et al., 2005) (pg. 95). Thus, in the prediction of transport properties, one may use the above theory to create a reference point from which the properties of liquids may be predicted. Corresponding states methods are especially popular for hydrocarbons but are very often not applicable to the more complex compounds with sufficient reliability (Assael et al., 1998). They form a firm basis from which other empirical or semi-empirical predictive methods may be developed.

- Molecular dynamics (MD) or molecular simulation methods are computational methods which attempt to simulate the real behaviour of compounds and calculate their physical properties via approximations of known physics. They are based on statistical mechanics and normally involve simultaneously solving the equations of motion for a system of atoms interacting with a given potential. However, a lack of sufficient computational power limited these and other early simulations to systems with a very small number of atoms and a bigger integration time step for chemical potential evaluations. In the past few decades, however, the number of MD studies has increased due to rapid advancements in computer speed and memory technology. It is now possible, using parallel computation on fast computer clusters, to model systems in the order of a million atoms (Hoover, 1991). Moreover, different types of chemicals require different simulation models. Reliable molecular models are required for the different types of chemicals; otherwise invalid results may be obtained. Due to the rapidly increasing available computing power, molecular simulation in combination with molecular modelling is becoming an interesting option for obtaining transport properties, however this has been limited to simple liquids such as CO₂ and C₂H₆ and complex fluids such as SF₆ and C₂F₆.

The empirical correlated model by Sato and Riedel (1977) (Horvath, 1992), which requires the temperature, critical temperature, and molecular weight for prediction of thermal conductivity of any organic compound was found by Horvath (Horvath, 1992) to be the best general correlation. A simpler correlation by Lakshmi and Prasad (Lakshmi and Prasad, 1992), based on the reference substance approach, whereby a compound for which accurate experimental data is available is used as a reference for the trend followed by the property under investigation, only requires the temperature and molecular weight as input.

Mathias et al. (Mathias et al., 2002) presented a model that may be used for the correlation of experimental data or for the prediction of thermal conductivity for pure fluids and mixtures using component specific parameters based upon an equation of state. The model utilizes the extended corresponding states model by Ely and Hanley (Ely and Hanley, 1983) but is also able to describe the critical enhancement contribution for pure fluids.
Corresponding states prediction, such as the model by Ely and Hanley (Ely and Hanley, 1983), take into account the state dependencies of temperature and density. Models using the corresponding states approach normally seem highly complex but are simple to apply, typically requiring state properties, critical properties and acentric factor.

As stated above very few methods take into account the pressure dependence of thermal conductivity. Lenoir (1957) and Missenard (1970) correlated the pressure effect on thermal conductivity and represented it in graphical form (Poling et al., 2004). Latini and Baroncini (1983) extended their low pressure equation to include pressures greater than a reduced pressure of 0.5 with three simple equations (Poling et al., 2004).

2.6. Group Contribution Methods

2.6.1. Robbins and Kingrea (1962)

Robbins and Kingrea (Reid et al., 1977) based their correlation upon the equation of Weber (1880) (Horvath, 1992) which gave the relationship between thermal conductivity and the liquid heat capacity at a standard temperature of 298 K. The liquid heat capacity was used to represent the temperature dependency and to provide a reference from which thermal conductivity could be predicted.

This method was based on previous work undertaken by Sakiadis and Coates (Sakiadis and Coates, 1955, Sakiadis and Coates, 1957) who developed a simple method to predict the results obtained from their experimental work. In their work contributions of functional groups were calculated at a reduced temperature of 0.6. However, Robbins and Kingrea utilise structural groups which are not dependent upon any state property and thus follow a proper group contribution scheme.

The equation developed took the following form:

\[
\hat{\lambda}_L = \frac{(88.0 - 4.94 H)(10^{-3})}{\Delta S^*} \left( \frac{0.55}{T_r} \right)^N C_p \rho^{4/3}
\]

\[(2.8)\]

\[
\Delta S^* = \frac{\Delta H_{eb}}{T_b} + R \ln(273/T_b)
\]

\[(2.9)\]

where

- \(\Delta S^*\) is the entropy of vaporization;
- \(C_p\) is the molar heat capacity;
- \(\rho\) is the molar density;
- \(T_r\) is the reduced temperature for the liquid of interest;
- $\Delta H_{vb}$ is the heat of vaporisation at the normal boiling point;
- $T_b$ is the normal boiling point.
- $N$ is set as one if the density of the liquid at 293 K is less than 1.0 g/cm$^3$ or as zero otherwise;
- $H$ is the group contribution parameter.

The group contribution parameter $H$ depends upon the molecular structure of the compound and may be calculated using functional group contributions based upon a set of 16 individual functional groups. The H-factor contributions are additive for compounds containing multiple functional groups as per the group contribution additivity concept.

The only problem with use of this method is that the required data for more complex compounds may not be readily available or available but not very accurate. This method shall not be further considered in this project.

### 2.6.2. Nagvekar and Daubert (1987)

This method is based upon the second order contribution scheme as set out by Benson and Buss (1958) (Nagvekar and Daubert, 1987), which was based upon "nearest neighbour interactions". This states that elements within a molecule are affected by neighbouring elements but that this effect decreases with distance. Thus using this definition, functional groups may be defined for the group contribution scheme.

The model expanded upon the linear temperature dependency of thermal conductivity which was found to be followed by most organic liquids. A study of experimental data by the authors showed that this trend was almost linear below the normal boiling point of the compound; however it curved slightly as the temperature exceeded the normal boiling point. Water and polyols were stated to be an exception to the rule (Nagvekar and Daubert, 1987). This is shown later on to be the case as water and polyols follow a different trend as compared to most organic hydrocarbons.

The model of Reidel (Reidel, 1951) was found to be applicable over a wider temperature range than a simple linear model; being applicable below and above the normal boiling point. Therefore, the temperature dependent equation was used as a basis for the group contribution model to be developed.

$$\lambda = A \left[ 1 + \frac{20}{3} \left( 1 - T_r \right)^{2/3} \right]$$

(2.10)

where $\lambda$ is the liquid thermal conductivity, $T_r$ the reduced temperature, and $A$ is a regressed constant dependent upon the class of liquid. This equation was modified and used in the following form:

$$\lambda = A + B (1 - T_r)^{2/3}$$

(2.11)
where A and B are the group contribution parameters. A total of 84 groups and 8 group corrections were used. The method is applicable within a temperature range of 0.3<T<0.9. The method does not account for unsaturated hydrocarbons very well. Although it was the first full group contribution method for thermal conductivity prediction, it seems to be the best method available in literature when compared to the other group contribution methods within this study. The only limitation to the method is its small range of applicability. From the training set of over 330 compounds used in the development of the new model, results could be predicted for only 206 compounds using this method. This may be attributed to restrictive definitions being used for structural groups.

Figure 2.9: Liquid thermal conductivity vs. temperature for trichloroethylene (data from the DDB (Gmehling et al., 2009))

Compared to other group contribution model equations available in literature, Eqn. (2.11) correlates with experimental data for most organic compounds with high accuracy. However, as can be seen from Figure 2.9 and Table 2.1, this is not true for the more complex organic compounds. The exponent of two thirds was carried over into the new model due to its usage within the Reidel model (Reidel, 1951) to account for a slight curvature noted within most experimental thermal conductivity vs. temperature curves above the normal boiling point. Optimisation of the value of the exponent utilizing a collection of experimental thermal conductivity data may yield a value which would reduce the overall prediction error. However, this term would maybe increase the predicted error for compounds which do not follow the expected curvature.
Table 2.1: Relative mean deviations (RMD) of liquid thermal conductivity for selected compounds using the Nagvekar and Daubert (1987) method (NP = Number of data points)

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>RMD (%)</th>
<th>NP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.56</td>
<td>65</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>10.16</td>
<td>52</td>
</tr>
<tr>
<td>2-Butanol</td>
<td>7.19</td>
<td>9</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>15.16</td>
<td>18</td>
</tr>
<tr>
<td>Methyl Isobutyl Ketone</td>
<td>10.92</td>
<td>9</td>
</tr>
<tr>
<td>m-Cresol</td>
<td>1.36</td>
<td>7</td>
</tr>
</tbody>
</table>

2.6.3. Assael, Charitidou & Wakeham (1989)

A semi-empirical model was developed using the group contribution scheme. Most prediction models previously published were based upon correlative methods with little or no basis in theory due to the lack of kinetic theory to explain this transport phenomenon. In this paper, the Enskog theory for hard-sphere molecules was applied to the van der Waals model for dense-fluid to yield an equation based upon the molar volume \( V \) and state temperature \( T \) for specific organic liquids:

\[
\lambda^* = 1.9362 \times 10^7 \left( \frac{M}{RT} \right)^{1/2} \lambda V^{2/3}
\]  
\[\text{(2.12)}\]

Eqn. (2.12) may be used to calculate the dimensionless thermal conductivity \( \lambda^* \) using experimental data. Based upon the aforementioned dense fluid model, Assael et al. (1989) derived a model relating the dimensionless thermal conductivity to the molar volume:

\[
\ln \lambda^* = 4.8991 - 2.2595 \ln \left( \frac{V}{V_O} \right)
\]  
\[\text{(2.13)}\]

In Eqn. (2.13) \( V \) is the molar volume and \( V_O \), the group contribution parameter is the characteristic molar volume of the liquid.

Regression for \( V_O \) was undertaken using Eqns. (2.12) and (2.13), yielding a linear temperature dependence and a non-linear but smooth dependence upon the number of carbons in the compound. Based upon the results a simple contribution scheme was proposed for prediction of \( V_O \) as follows:

\[
V_O = V_O^N + V_O^{1H} + V_O^{1OH} + V_O^{2OH}
\]  
\[\text{(2.14)}\]

The first term represents the contribution of a straight chain of carbon atoms; the second term is the contribution for a benzene ring; the third term represents the contribution of a hydroxyl bond and the fourth term represents the contribution of a second hydroxyl bond within the compound. The regression was based upon 14 compounds with 715 data points. The problem of utilizing so few
compounds in the training set is that the method may work extremely well for the training set and compounds similar to those in the training set, but badly for other compounds not included in the training set.

The binary interaction parameters for the four contribution schemes for $V_o$ were calculated using the group contribution method and are shown in Table 2.2. The contribution scheme for the four contributions of Eqn. (2.14) are represented below as the non-linear dependence upon the number of carbon atoms mentioned previously:

$$10^6 V_o^N (\theta, n_c) = \sum_{i=0}^{2} \sum_{j=0}^{3} a_{ij} n_c^i \theta^j$$  \hspace{1cm} (2.15)

$$10^6 V_o^{1B} (\theta, n_c) = \sum_{i=0}^{1} \sum_{j=0}^{1} b_{ij} n_c^i \theta^j$$  \hspace{1cm} (2.16)

$$10^6 V_o^{1OH} (\theta, n_c) = \sum_{i=0}^{1} \sum_{j=0}^{2} c_{ij} n_c^i \theta^j$$  \hspace{1cm} (2.17)

$$10^6 V_o^{2OH} (n_c) = \sum_{j=0}^{1} d_j n_c^j$$  \hspace{1cm} (2.18)

Table 2.2: Coefficients for use in Eqns. (2.15) to (2.18) (m$^3$.mol$^{-1}$) (Assael et al., 1989)

<table>
<thead>
<tr>
<th>$i$</th>
<th>$j$</th>
<th>$a_{ij}$</th>
<th>$b_{ij}$</th>
<th>$c_{ij}$</th>
<th>$d_j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>6.3918</td>
<td>-14.700</td>
<td>-0.1630</td>
<td>4.40</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>9.7389</td>
<td>-2.8280</td>
<td>-4.5280</td>
<td>0.70</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>0.84785</td>
<td>-</td>
<td>0.7807</td>
<td>-</td>
</tr>
<tr>
<td>0</td>
<td>3</td>
<td>-0.013132</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>8.1945</td>
<td>1.7209</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>-4.57722</td>
<td>-0.52991</td>
<td>4.4797</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>0</td>
<td>-</td>
<td>-0.69653</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1.4055</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
The group contributions \(a_{ij}, b_{ij}, c_{ij}\) and \(d_{ij}\), were determined to represent the effect of a structural group upon its neighbours and are given in Table 2.2. The dimensionless temperature \(\Theta\) is defined as \(T/273.15\) and \(n_c\) is the total number of carbon atoms in the compound of interest.

The model may only be used for straight chain carbon compounds. However, the compound may contain a maximum of two hydroxyl groups, one benzene ring and no double bonds. Moreover, the model may only be used for straight chain alkanes, aromatic hydrocarbons, alcohols, cyclic alcohols, diols and water. The method is applicable within a temperature range of 110 to 370 K and for pressures up to 600 MPa.

Due to the limited range of applicability to organic compounds, the method was not considered in the development of the new model. Consequently, the method was not tested against the six compounds as undertaken for other methods.

2.6.4. Sastri and Rao (1993)

Sastri and Rao proposed a method, which was applicable to a wider range of organic liquids than other group contribution methods available at the time. It covers the saturated liquid region from the triple point to a reduced temperature of 0.95. In contrast to other methods, where the temperature dependency was based on the critical temperature, the normal boiling point was used for correlating the temperature dependency as it was found by the authors to lie approximately midway between the triple point and the critical point in many instances.

Moreover, critical property data is not widely available for all the compounds of interest, especially in case of new compounds. Although prediction methods are widely available, their accuracies are subjective to the training sets used for model development.

Analysis of data again revealed the linear dependence of thermal conductivity on temperature, which was followed by most organic liquids with the exceptions being organic liquids containing multiple hydroxy groups. This agreed with the dependency found by Nagvekar and Daubert (Nagvekar and Daubert, 1987).

Parameter regression was based upon experimental data for 37 organic liquids by Miller (1976) (Sastri and Rao, 1993). Analysis of the experimental data yielded two separate relationships for the thermal conductivity of organic liquids above and below the liquid boiling point. The model is as follows:

\[
\lambda = \lambda_B \left(\frac{T_B}{T}\right)^{0.5}, \quad T \leq T_B
\]

\[
\lambda = \lambda_B \left(\frac{T_B}{T}\right)^{1.15}, \quad T \geq T_B
\]
Here, $\lambda_n$ is the thermal conductivity at the normal boiling point and it is calculated using group contributions. It was noted that this value was the same for all liquids of the same series at their respective boiling points. The exponent values 0.5 and 1.15 are regressed values which are constant for all liquids below and above the boiling points respectively. During evaluation of experimental data for the current model, different trends for data above and below the boiling point were not found.

Although providing 29 groups and 6 group corrections, the results, as shown in Figure 2.10 and Table 2.3 below, indicate that the method does not work very well for more complex hydrocarbons, nitrogen, oxygenated and halogenated compounds. This may be attributed to more complex chemical interactions occurring due to a larger number of bonds within the compounds. The general good results provided with the use of only a small number of groups is a good example for the predictive ability of a group contribution method for physical property data.

![Graph showing liquid thermal conductivity vs. temperature for trichloroethylene](image)

**Figure 2.10: Liquid thermal conductivity vs. temperature for trichloroethylene (data from the DDB (Gmehling et al., 2009))**

**Table 2.3: Relative mean deviations (RMD) of liquid thermal conductivity for selected compounds using the Sastri and Rao (1993) method (NP = Number of data points)**

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>RMD (%)</th>
<th>NP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>10.87</td>
<td>65</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>7.64</td>
<td>52</td>
</tr>
<tr>
<td>2-Butanol</td>
<td>2.65</td>
<td>9</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>1.49</td>
<td>18</td>
</tr>
<tr>
<td>Methyl Isobutyl Ketone</td>
<td>18.63</td>
<td>9</td>
</tr>
<tr>
<td>m-Cresol</td>
<td>6.80</td>
<td>7</td>
</tr>
</tbody>
</table>
2.6.5. Rodenbush, Viswanath & Hsieh (1999)

The primary goal of this work was to predict the thermal conductivity of vegetable oils and its resulting affect on the Prandtl number. The group contribution model was based upon the semi-theoretical method derived by Viswanath and Klaas (Klaas and Viswanath, 1998),

$$\frac{\lambda}{\lambda_o} = \left(\frac{T}{T_o}\right)^{-2/3} \quad (2.21)$$

The problem with Eqn (2.21) is that it was designed to work only between the melting point and normal boiling point, as temperatures higher than the normal boiling point lead to decomposition for vegetable oils and is not of interest.

The above model was derived from the original relationship given by Horrocks and McLaughlin (Horrocks and McLaughlin, 1963) which was based on the vibrational theory of thermal conductivity, which assumed that a liquid is composed of “spherically symmetric molecules”. The relationship proposed was:

$$\lambda = 2p\nu mlC_v \quad (2.22)$$

In this relationship, $p$ is the probability of energy transfer on collision, $\nu$ is the vibrational frequency, $m$ is the number of molecules per unit area, $l$ is the distance between adjacent planes and $C_v$ is the specific heat per molecule (Horrocks and McLaughlin, 1963). According to Eqn. (2.22), the relationship describes the possibility of transfer of the total amount of heat of all the molecules within the compound in a given area with other molecules on collision.

Using Eqn. (2.21) as a starting point, Rodenbush and co-workers combined the constants in the equation:

$$\lambda = \left(\frac{\lambda_o T_o^{2/3}}{T}\right) \times T^{-2/3} \quad (2.23)$$

Thus a simplistic equation with a theoretical basis for the prediction of thermal conductivity via the bond contribution method was developed:

$$\lambda = DT^{-2/3} \quad (2.24)$$

In Eqn. (2.24) $D$ is the lumped constant $\frac{\lambda_o T_o^{2/3}}{T}$ and it was proposed that this value could be predicted for the different components using bond contributions and corrections. Model regression was performed using 228 liquids with 1487 experimental data points, for 84 bond contributions and 10 corrections. The average absolute error reported by the authors for the model was 2.5%. Due to the simplicity of the model, it correlates data of simple trends to a high accuracy as shown in Figure 2.11 below.

Sastri and Rao proposed a new equation similar to the Rackett equation for densities (Sastri and Rao, 1999). Their proposed group contribution method for density predictions provided a large improvement in predicted results compared to previous forms, thus a similar form of their density equation was proposed for use in modelling the thermal conductivity vs. temperature relationship. It was noted in a previous work (Sastri and Rao, 1993) that at temperatures above the normal boiling point the trend followed by thermal conductivity deviated from the basic linear model. Therefore, based upon the previously derived density equation utilised for saturated organic liquid volume prediction (Sastri et al., 1997) and the trend followed by previous thermal conductivity models from literature (Nagvekar and Daubert, 1987, Sakiadis and Coates, 1955, Sakiadis and Coates, 1957, Sastri and Rao, 1993), the following temperature to thermal conductivity relationship was assumed:

$$\lambda = MN^{(1-T)}$$

(2.25)

The constants M and N were defined as being dependent upon the compounds and n an index that should be constant for all liquids. The equation was then expanded upon to define the pseudo critical ($\lambda_c^*$) and normal boiling point ($\lambda_B$) thermal conductivities:

$$\lambda = \lambda_c^* \left[ \frac{\lambda_B}{\lambda_c^*} \right]^{(1-T)/(1-T_B)}$$

(2.26)

In Eqn. (2.26), $T_B$ is defined as $T_B/T_c$. Then, using the Eqn. (2.26) and defining the ratio of $\lambda_c^*/\lambda_B$ as the constant ‘$a$’, the final model equation was derived:

![Figure 2.11: Liquid thermal conductivity vs. temperature for cyclopentane (data from the DDB (Gmehling et al., 2009))](image)
\[ \lambda = \lambda_B a^b \]  
\[ b = \left[ 1 - \left( \frac{[1-T_c]}{[1-T_r]} \right)^n \right] \]  

In this equation, \( \lambda_B \) is calculated using the group contribution method:

\[ \lambda_B = \sum \Delta \lambda_g + \sum \Delta \lambda_{corr} \]  

In Eqn. (2.29) \( \Delta \lambda_g \) is the group contribution value of the different constituent groups and \( \Delta \lambda_{corr} \) is a correction factor, which may be required for some compounds. The correlated constants ‘\( a \)’ and ‘\( n \)’ were found to be constant for almost all compounds (\( a = 0.160 \) and \( n = 0.20 \)) with the exception of alcohols and phenols where they were found to be higher (\( a = 0.856 \) and \( n = 1.23 \)). The two correlated constants help account for the hydrogen bonding in the alcohols and phenols, as seen in Table 2.4, which normally result in predicted thermal conductivities being much higher than the experimental findings. This method uses 32 groups and 7 group corrections.

**Table 2.4: Relative mean deviations (RMD) of liquid thermal conductivity for selected compounds using the Sastri and Rao (1999) method (NP = Number of data points)**

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>RMD (%)</th>
<th>NP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>4.21</td>
<td>65</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>12.27</td>
<td>52</td>
</tr>
<tr>
<td>2-Butanol</td>
<td>7.28</td>
<td>9</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>2.44</td>
<td>18</td>
</tr>
<tr>
<td>Methyl Isobutyl Ketone</td>
<td>13.76</td>
<td>9</td>
</tr>
<tr>
<td>m-Cresol</td>
<td>2.38</td>
<td>7</td>
</tr>
</tbody>
</table>

![Figure 2.12: Liquid thermal conductivity vs. temperature for cyclopentane (data from the DDB (Gmehling et al., 2009))](image-url)
The main problem with the new model, as seen in Figure 2.12 above, is that, although it works very well for correlating organic molar liquid volumes, it does not correlate thermal conductivity data very well. However, the new method combined with the previously published method for predicting thermal conductivity below the boiling point, is able to predict thermal conductivity for the entire saturated liquid region from the triple point to close to the critical point.

Implementation of the method within this work was not undertaken as construction of a group definition (".ink") file could not be done properly, as the published paper (Sastri and Rao, 1999) did not contain enough data to determine group priorities and family corrections.

2.7. **Corresponding State Methods**

2.7.1. Ely and Hanley (1983)

A model for the prediction of thermal conductivity over the entire range of PVT states was developed by Ely and Hanley (1983). This model is based on the extended corresponding states theory, resulting in a set of equations requiring the critical constants, molecular weight, the ideal heat capacity at constant pressure for each component (for representation of internal degrees of freedom), and the acentric factor. The method is applicable only to non-polar pure fluids and their mixtures.

The method assumes that the properties of a single-phase mixture may be related to that of a hypothetical pure fluid, which may then be estimated using the corresponding states theory. The background contribution for thermal conductivity ($\lambda$) is assumed to be divided into two contributions, the first being that for the effect of internal degrees of freedom ($\lambda^i$) and the second being that due to translational or collision effects within the molecule ($\lambda^t$).

$$\lambda = \lambda^i + \lambda^t$$ (2.30)

The corresponding states method used by Ely and Hanley assumes the transfer of energy due to internal degrees of freedom may be calculated via the modified Eucken correlation for polyatomic gases (in which the energy is assumed independent of density):

$$\frac{\lambda^i M_\alpha}{\eta^*_\alpha} = 1.32(C_{p,\alpha}^0 - \frac{5R}{2})$$ (2.31)

In the above equation $\lambda^i_\alpha$ is the contribution due to internal degrees of freedom for pure component $\alpha$, $M_\alpha$ is the molecular weight, $\eta^*_\alpha$ is the dilute gas viscosity, $C_{p,\alpha}^0$ is the ideal gas heat capacity at constant pressure and $R$ is the gas constant. For a mixture, the empirical mixing rule by Li (1976) may be used:
\[ \hat{\lambda}_{\text{mix}}(T) = \sum_{\alpha} \sum_{\beta} x_{\alpha} x_{\beta} \hat{\lambda}_{\alpha\beta} \]  
(2.32)

where

\[ \hat{\lambda}_{\alpha\beta} = 0.5 \left( \left( \hat{\lambda}_{\alpha} \right)^{-1} + \left( \hat{\lambda}_{\beta} \right)^{-1} \right)^{-1} \]  
(2.33)

The translational effect is calculated using the corresponding states theory, assuming a hypothetical pure fluid if calculations for a mixture are being undertaken:

\[ \hat{\lambda}_{\text{mix}}(\rho, T) = \hat{\lambda}_{\alpha}(\rho, T) = \hat{\lambda}_{\alpha}(\rho_0, T_0) F_{\lambda} \]  
(2.34)

The subscript “0” is used for the corresponding states reference fluid and the equivalent density and temperature are represented using the relations:

\[ \rho_0 = \rho h_{x,0} \text{ and } T_0 = Tf_{x,0} \]  
(2.35)

In addition, the function \( F_{\lambda} \) is a function of corresponding states theory reducing ratios:

\[ F_{\lambda} = \left( \frac{M_0}{M_x} \right)^{1/2} f^{1/2} x_{x,0}^{-2/3} \]  
(2.36)

where \( M_x \) is given by the following mixing rule:

\[ M_x^{1/2} f_{x,0}^{1/2} h_{x,0}^{-4/3} = \sum_{\alpha} \sum_{\beta} x_{\alpha} x_{\beta} M_{\alpha\beta}^{1/2} f_{\alpha\beta}^{1/2} h_{\alpha\beta}^{-4/3} \]  
(2.37)

with

\[ M_{\alpha\beta} = 2 \left( M_{\alpha}^{-1} + M_{\beta}^{-1} \right)^{-1} \]  
(2.38)

The reducing ratios are defined by the following mixing rules:

\[ f_{x,0} h_{x,0} = \sum_{\alpha} \sum_{\beta} x_{\alpha} x_{\beta} f_{\alpha\beta} h_{\alpha\beta} \]  
(2.39)

\[ h_{x,0} = \sum_{\alpha} \sum_{\beta} x_{\alpha} x_{\beta} h_{\alpha\beta} \]  
(2.40)

\[ f_{\alpha\beta} = \left( f_{\alpha} f_{\beta} \right)^{1/2} (1 - k_{\alpha\beta}) \]  
(2.41)

\[ h_{\alpha\beta} = \frac{1}{8} \left( h_{\alpha}^{1/3} + h_{\beta}^{1/3} \right)^3 (1 - l_{\alpha\beta}) \]  
(2.42)
Moreover, the pure property reducing ratios are given by the following equations:

\[
f_a = \Theta_a(T_r^\alpha, V_r^\alpha, \omega_a) \times (T_c^\alpha N_c^0) \tag{2.43}
\]

\[
h_a = \Phi_a(T_r^\alpha, V_r^\alpha, \omega_a) \times (V_c^\alpha N_c^0) \tag{2.44}
\]

In the above two equations, \( \Theta_a \) and \( \Phi_a \) are shape factors, which were defined previously by Ely and Hanley. The equations use binary interaction parameters \( k_{\alpha\beta} \) and \( l_{\alpha\beta} \), which may be adjusted for better correlation and ensuing prediction. The state reference fluid of Eqn. (2.34) may be calculated using extensive equations as laid out by Ely and Hanley, which includes a correction factor based on the modified Enskog theory to account for non-correspondence.

Despite the complicated relationships for representation of mixtures, the model is simplistic in its representation of pure fluids. The model cannot be used for prediction of data but only for the correlation of experimental data. The model may be used for interpolation and extrapolation of data for compounds for which regressed parameters are available.

### 2.8. Empirical Correlations

#### 2.8.1. Sato and Reidel (1977)

In 1973, Sato (Reid et al., 1977) proposed an empirical relationship based upon a compound’s molar weight for the prediction of thermal conductivity at the normal boiling:

\[
\lambda_{rb} = \frac{2.64 \times 10^{-3}}{M^{1/2}} \tag{2.45}
\]

Combining the method by Sato with that by Reidel (Reidel, 1951), a new correlation which used thermal conductivity at the normal boiling point as a reference point, was proposed:

\[
\lambda = \frac{2.64 \times 10^{-3}}{M^{1/2}} \frac{3 + 20(1-T_r)^{2/3}}{3 + 20(1-T_{rb})^{2/3}} \tag{2.46}
\]

In Eqn. (2.46) \( M \) is the molecular weight, \( T_r \) is the reduced temperature and \( T_{rb} = T_b/T_c \), where \( T_b \) is the normal boiling point and \( T_c \) is the critical temperature. The method was said to be applicable from the triple point up to a reduced temperature of 0.95.

The model produced fairly accurate results for most compounds as shown in Table 2.5 below.
Table 2.5: Relative mean deviations (RMD) of liquid thermal conductivity for selected compounds using
the Sato and Reidel (1977) method (NP = Number of data points)

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>RMD (%)</th>
<th>NP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.62</td>
<td>65</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>7.16</td>
<td>52</td>
</tr>
<tr>
<td>2-Butanol</td>
<td>14.56</td>
<td>9</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>8.86</td>
<td>18</td>
</tr>
<tr>
<td>Methyl Isobutyl Ketone</td>
<td>9.35</td>
<td>9</td>
</tr>
<tr>
<td>m-Cresol</td>
<td>5.14</td>
<td>7</td>
</tr>
</tbody>
</table>


The reference substance approach, which uses a compound with accurate and precise experimental
data as a reference point for further property prediction, was the basis for the development of a simple
empirical correlation for the prediction of thermal conductivity. Review of previous prediction
methods showed that many are based upon transport properties that may not be readily available, thus
a method was to be created based upon the molecular mass of the compound, which is easily
calculated for all compounds.

The authors chose benzene as the reference compound based upon the availability of a large amount of
accurate data allowing accurate modelling of the close to linear trend followed by thermal
conductivity. Thermal conductivity data for various compounds were then plotted against those for
benzene and fitted using the following linear model:

\[ \lambda = m \lambda_B + c \] (2.47)

The resulting slopes \( m \) and intercepts \( c \) were then fitted to the compound’s molecular mass. The
temperature dependency for the model was represented using the benzene thermal conductivity
temperature dependency:

\[ \lambda_B = -0.00035T + 0.25115 \] (2.48)

Combining Eqns. (2.48) and (2.47) with the fitted molecular mass relationships for \( m \) and \( c \), the
resulting empirical equation was derived for easy thermal conductivity prediction:

\[ \lambda = 0.0655 - 0.0005T + \frac{1.3855 - 0.00197T}{M^{0.5}} \] (2.49)

It was found that the simpler method of Lakshmi and Prasad produced lower errors than most other
empirical models. The advantage of the method, represented in Eqn. (2.49), is that it only requires a
compounds molecular weight to provide structural representation.
Table 2.6: Relative mean deviations (RMD) of liquid thermal conductivity for selected compounds using the Lakshmi and Prasad (1992) method (NP = Number of data points)

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>RMD (%)</th>
<th>NP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.94</td>
<td>65</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>5.00</td>
<td>52</td>
</tr>
<tr>
<td>2-Butanol</td>
<td>5.99</td>
<td>9</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>8.80</td>
<td>18</td>
</tr>
<tr>
<td>Methyl Isobutyl Ketone</td>
<td>4.97</td>
<td>9</td>
</tr>
<tr>
<td>m-Cresol</td>
<td>16.94</td>
<td>7</td>
</tr>
</tbody>
</table>

However, as it is based on the reference substance approach with no grounding in critical data theory, when applied to other compounds which follow slightly different trends due to more different molecular structures, the method would produce much larger errors. Examples of this would be halogen compounds with many branches, different substituents or different intermolecular bonding and is shown in Table 2.6 above for m-Cresol, whilst other compounds produce more accurate correlations.

2.8.3. **Mathias, Parekh and Miller (2002)**

Mathias *et al.* aimed at developing a model that would include the critical enhancement which occurs in the critical region and thus provide a model with improved usability for industry. The model was developed for prediction of thermal conductivity over all thermodynamic states from the dilute gas to the dense liquid regions. Based upon the work of Sengers (Millat *et al.*, 2005) and that of Ely and Hanley (Ely and Hanley, 1983), thermal conductivity was broken down into the background contribution and the contribution due to critical enhancements:

\[ \lambda = \bar{\lambda} + \Delta \lambda_c \] (2.50)

The background contribution was then broken down into two further contributions due to transfer of energy from purely collisional or translational effects and the transfer of energy due to the internal degrees of freedom as per Ely and Hanley (Eqn. (2.30)).

The background contribution was calculated as done by Ely and Hanley (Eqns. (2.30) to (2.44)). The shape factors (\( \theta \) and \( \phi \)) are represented as:

\[ \theta_{\lambda_u} = 1 + \theta_{\lambda_u1} + \theta_{\lambda_u2} \ln(T_{\lambda_u}) + \theta_{\lambda_u3} \left(1 - \frac{1}{T_{\lambda_u}}\right) \] (2.51)

\[ \phi_{\lambda_u} = 1 + \phi_{\lambda_u1} + \phi_{\lambda_u2} \ln(T_{\lambda_u}) + \phi_{\lambda_u3} \left(1 - \frac{1}{T_{\lambda_u}}\right) \] (2.52)
The coefficients in the shape factor equations, according to Ely and Henley, may be adjusted for producing an accurate description of thermal conductivity. Details and numerical values of all correlated parameters can be found in Appendix C. The shape factors are functions of temperature and density but were found by Mathias and co-workers to be sufficiently represented as a function of temperature only. Using the Peng-Robinson equation of state, and methane as the reference fluid, the coefficients were regressed to the following equations for representation of polar and non-polar fluids using the acentric factor to represent the properties of the compounds of interest:

\[ \theta_{\alpha_1} = 0.591 \times (\omega_\alpha - \omega_0) \]  \hfill (2.53)

\[ \theta_{\alpha_2} = 0.420 \times (\omega_\alpha - \omega_0) \]  \hfill (2.54)

\[ \theta_{\alpha_3} = 0 \]  \hfill (2.55)

\[ \phi_{\alpha_1} = 0.945 \times (\omega_\alpha - \omega_0) \]  \hfill (2.56)

\[ \phi_{\alpha_2} = -0.184 \times (\omega_\alpha - \omega_0) \]  \hfill (2.57)

\[ \phi_{\alpha_3} = 0 \]  \hfill (2.58)

The critical enhancement factor was represented by a simple correlation:

\[ \Delta \lambda_c = a \delta^{-b} \]  \hfill (2.59)

In Eqn. (2.59), \( a \) and \( b \) are parameters which may be used to achieve an optimum correlation of data in the vicinity of the critical point. The function \( \delta \) is a dimensionless value referred to as the bulk modulus. It is a measure of a compound’s resistance to compression and thus especially small in the region around the critical point.

The bulk modulus is used in Eqn. (2.59) to represent the divergence of thermal conductivity at the critical point. The bulk modulus is related to the inverse of the isothermal compressibility and with the use of an equation of state, such as the Peng-Robinson equation of state as used by the authors, may be determined for a pure fluid as follows:

\[ \delta = -\frac{V^2}{nRT} \left( \frac{\partial P}{\partial V} \right)_{T,n} = \frac{V}{P} \left( \frac{\partial P}{\partial V} \right)_{T,n} \]  \hfill (2.60)

For a multi-component mixture, the following mixing rules, using mole fraction averages, were used:

\[ \delta_{\text{mix}} = -\frac{V^2}{nRT} \sum \alpha x_\alpha \left( \frac{\partial P}{\partial V} \right)_{T,n,\rho,\mu_\alpha} \]  \hfill (2.61)
\[ n = \sum \alpha \]
\[ a = \sum \alpha \frac{x_a}{a} \]
\[ b = \sum \alpha \frac{x_b}{b} \]

Provided with fairly accurate experimental data, regression for the fitting coefficients for the set of equations laid out above may be undertaken to increase the accuracy for data correlation. The model may be used for prediction of pure component or mixture thermal conductivity when the fitting parameters of Eqns. (2.41) and (2.42) are set to zero. Critical enhancement may be accurately described by adjustment of the parameters ‘\(a\)’ and ‘\(b\)’.

The model by Mathias et al. may be the most accurate and flexible available for correlation of thermal conductivity. Prediction of both non-polar and polar compounds for a range of thermodynamic states from that of a dilute gas to that of a dense liquid may be performed using the model.

However, experimental data is required for the regression of the shape factors before the method may be used for prediction. If experimental data is not available, equations for calculating the coefficients for the shape factors are provided (Eqns. (2.53) to (2.58)). Refer to Appendix C for sample calculations and results for the application of the method as a predictive method to the training set used for development of the new method.

2.9. Summary

The first step in the development of a prediction method for a thermophysical property is the selection of an equation that must fit the experimental data sufficiently well without employing an excessive number of variables or input parameters. Temperature follows an almost linear trend for thermal conductivity thus indicating a simple model should suffice for development of the method.

There are numerous different general correlation methods available which are based on one or more pure component properties; an excellent review being provided by Horvath (Horvath, 1992). Corresponding state methods are the most widely used reference point prediction methods. Although especially popular for hydrocarbons, they are very often not applicable to the more complex compounds with sufficient reliability (Assael et al., 1998). However, as group contribution methods tend work from a point of reference, a good starting point would be a corresponding states method such as was undertaken by Mathias et al. (2002).

From the available group contribution methods, only those of Nagvekar and Daubert (1987), and Sastri and Rao (1993) were considered in this work. This led to the idea of using a simple linear
equation, for a reference point predictive method. As may be seen in the works of Nagvekar and Daubert (1987), and Sastri and Rao (1993), the normal boiling point is the most preferable reference point due to the divergence of thermal conductivity at the critical point.
3. Computation and Database Tools

3.1. Database

The experimental data used in the development of the new model and for regression of model parameters was obtained from the Dortmund Data Base (DDB) (Gmehling et al., 2009). The DDB contains over 100 000 thermal conductivity data points for almost 900 components for various physical states viz. solid, liquid, and gas. The advantage of using such a large database is that it allows a model to have a greatly increased range of applicability.

The data used from the DDB was stored in a Microsoft Access database. This increased the ease in which data was accessed and manipulated. Filters available within Access were used for data selection and outliers or unreliable data were flagged in the databank tables.

The manipulation of data was performed using Visual Basic for Applications (VBA) in Microsoft Excel. This was achieved via the creation of VBA interfaces within Excel using Microsoft ActiveX Data Objects (ADO) from VBA to communicate with the database for retrieval and storage of experimental data. The access of data from the database was performed using Structured Query Language (SQL) to define and filter what data was retrieved from the database.

3.2. Data validation

The experimental thermal conductivity data obtained from the DDB (Gmehling et al., 2009) consisted of a data set of 100515 data points for 867 components. This data set consisted of a collection of pure component experimental data for the various phases, viz. solid, liquid and vapour. The temperature of the data points ranged from sub-critical to super-critical conditions. The thermal conductivity database within the DDB (Gmehling et al., 2009) is currently one of the largest collections of experimental thermal conductivity data available containing data collected from papers dating from as early as the 1880’s. Utilizing this data would allow one to identify trends and relationships with greater accuracy and certainty than with the smaller datasets which were used in previous methods.

Before work on a model could be undertaken, the experimental data were filtered to establish which data points would be used in the training set. Built-in filters within the database were utilised in conjunction with new filters created using SQL code to retain liquid phase data for organic liquids within the temperature range from the melting or triple point up to the critical point. The resultant data set contained almost 46000 data points for 474 components of which ~73 % was for higher pressure systems (pressure greater than 1.5 atm) and the rest for pressures below 1.5 atm.

Figure 3.1 below shows all experimental data for cyclohexane. It can be seen that there are very few black data points on the graph (representing data at 1 atmosphere) as compared to green data points which indicate data at an elevated pressure.
It should be noted that the data was collected from eighteen different journals in literature dating from 1957 to 2004 (Gmehling et al., 2009). In Figure 3.1, a number of data points at 1 atm give significantly higher (up to 20%) thermal conductivity than the majority of low pressure data. These values are from older publications (before 1963), while all lower values were measured after 1978. Therefore, when looking at the entire DDB (Gmehling et al., 2009) database, the age of the experimental data seems to be relevant.

To further illustrate this, Figure 3.2 shows the thermal conductivity of liquid toluene at 25 °C as measured by different authors from the 1920’s to the early 1990’s.
A clear trend is evident in the thermal conductivity as a function of the year of measurement. Heat transfer consists of both conduction and convection, whereby both occur naturally. To measure the thermal conductivity which is a measurement of the heat transfer due to conduction only, convection and radiation will have to be eliminated. The trend displayed in Figure 3.2 above, could thus be used as an indication of the improvement of the equipment and methods used in liquid thermal conductivity experiments showing this gradual elimination. Therefore, when validating data for the training set, most data from before 1960 were flagged and removed.

Due to the numerous factors mentioned above, it was decided that selection of the experimental data would have to consist of multiple steps as follows:

1. Identify, flag and remove data significantly above one atmosphere but not at the saturation curve.
2. Filter data for components for which three data points or less are available and flag them as they will not be used in the regression.
3. Visually verify remaining data to identify outliers and erroneous data sets, and
4. Undertake regression to determine where erroneous data or trends might have been missed during visual verification.

As per the first point, selection of the data was undertaken with data at saturation conditions or at a pressure of one atmosphere being retained only. Where data above the normal boiling point was not available, thermal conductivity at one atmosphere was extrapolated from the high pressure data (when accurate high pressure data was available for this task) and employed in the regression. This was undertaken on the assumption that the error between the associated saturated pressure thermal conductivity and the thermal conductivity at one atmosphere would be small enough to warrant an omission.

To show the validity of this assumption, calculations are undertaken using data for 1-octene from the DDB (Gmehling et al., 2009). The critical temperature for 1-octene is 566.6 K. The temperature selected is 500 K.

As shown in Figure 3.3, at 500 K the saturation pressure is 989 kPa. The temperature of 500 K is at a reduced temperature of 0.88 which is much higher than the boiling point of 394.8 K at a reduced temperature of 0.7.
Pressure data for thermal conductivity was used to extrapolate for the thermal conductivity of 1-octene at one atmosphere and 500 K. This produced a thermal conductivity of \(0.0741 \text{ W.m}^{-1}\text{.K}^{-1}\). At 989 kPa and 500 K, a thermal conductivity of \(0.0749 \text{ W.m}^{-1}\text{.K}^{-1}\) was obtained. From Figure 3.4 below, it may be seen that these two thermal conductivities lie extremely close together (within the red circle) notwithstanding the large difference in pressure. The deviation between the two thermal conductivities is only 1.1 \%, which is smaller than most errors obtained from prediction models currently available. Steps two and three were undertaken on completion of the above.

---

**Figure 3.3:** Vapour pressure curve for 1-octene (data from DDB (Gmehling et al., 2009))

**Figure 3.4:** Liquid thermal conductivity vs. pressure for 1-octene at 500K (data from DDB (Gmehling et al., 2009))
However, to manually plot the data sets for over 400 compounds and then go through each plot verifying data would require a large amount of time and would thus become inefficient. To perform this task efficiently, multiple user interfaces which were created using Visual Basic were used (refer to Appendix D for screenshots of the user interfaces). Data points which did not follow trends and outliers, such as those seen in Figure 3.5 below, were flagged for removal once model regression occurred. By way of this method large amounts of data points were flagged and removed from the training set.

![Graph](image)

**Figure 3.5: Liquid thermal conductivity vs. temperature for cyclohexane (1atm - all data from DDB (Gmehling et al., 2009))**

The validation of data was performed using an iterative procedure. This method was used as the data for many of the components where highly scattered and/or contained multiple trends. An example of this is shown in Figure 3.5 for cyclohexane. To determine which of the trends were “correct”, all the data were initially correlated to the model equation. Next, the compound specific constants $A$ and $B$ were correlated to their respective group contribution schemes. The data from the trend which had the highest relative deviation compared to the rest of the data set were eliminated.

The correlation sequence was then undertaken again with the remaining data. The data points which provided the lowest relative mean deviation after model regression were kept for use in the training set. In cases where this method did not work, if data at higher pressures were available, the ‘pressure data’ were extrapolated to obtain the liquid thermal conductivity at one atmosphere. Final data employed within the training set followed trends as depicted in Figure 3.6 with almost 40% of the original training set data points flagged as either bad data or not following respective family trends.
Figure 3.6: Liquid thermal conductivity vs. temperature for cyclohexane showing the data used in the training set (1atm – data from DDB (Gmehling et al., 2009))

The next step in the process was to undertake the final correlation of the data to the model equation and subsequently, the correlation of the compound specific model equation constants to their respective group contribution schemes to determine the structural contributions for the group contribution predictive scheme. The method used for regression in determining the structural contributions and the correlation of the data to the model equation, all followed a simple linear regression algorithm.

3.3. Regression

The solution of N equations with N unknowns or coefficients is easily obtained. However when the system is over-determined, there may exist multiple solutions which could satisfy the equation set. Therefore, to obtain the “optimum” solution set, a regression, linear or non-linear, may be undertaken.

To obtain the optimum coefficients for the model equation, simple linear regression and weighted linear regression routines were used. The regression routines were coded using Visual FORTRAN and stored as DLL files during previous work done within the Thermodynamics Research Unit (Moller, 2007, Olivier, 2010). These methods are not the only ways in which the regression may be undertaken statistically but were the simplest and most efficient methods to be used as proven in previous work.

3.3.1. Linear regression

The modelling of any relationship between one or more variables denoted \( y \) and one or more variables denoted \( X \), such that \( y \) depends linearly on \( X \) with one or more unknown coefficients may be referred to as linear regression. It has many practical uses e.g. interpolation or extrapolation of data within a data set of \( y \) and \( X \) values, e.g. where \( y \) is dependent upon one variable only viz. \( y = y(X) \); or to
quantify the strength of the relationship between $y$ and multiple $X$ variables viz. $y = y(X_1, X_2, ..., X_i)$, whereby the relationships may be assessed and the variables which contain redundant information about $y$ identified (Wikipedia, 2010).

Linear models are often regressed using the approach known as the method of least squares. Although there are other ways by which coefficients may be regressed, this is the most commonly used method. The method is used to determine the solution/s of an over-determined system of equations whereby the sum of the square of the residual between the model and experimental points are used as the objective or error function.

$$F = \sum_{i=1}^{n} (Y_i - \bar{Y}_i)^2$$  \hspace{1cm} (3.1)

The objective function is used to determine when the optimum solution or best linear unbiased estimator of the coefficients is obtained. The solution occurs at $F_{\text{min}}$, which is the minimum sum of the squared residuals. The minimum is obtained by setting the gradient of the solution Eqn. (3.1) to zero and solving for the model parameters.

The final solution may be obtained from the least squares regression in the following matrix form:

$$A = (X^T X)^{-1} X^T y$$  \hspace{1cm} (3.2)

3.3.2. **Weighted linear regression**

When undertaking a correlation of experimental data, it is assumed that each data point provides equally precise information concerning the variation of the process. It is therefore assumed that the standard deviation of the error term is constant over all data points, viz. explanatory variables.

This assumption is not always valid in modelling of data. The best example would be the work undertaken in this thesis, as shown in Figure 3.7 below where the data is quite scattered. It may thus not be reasonable to assume that every observation should be treated equally. In a situation such as this, a weighting may be applied to the data in an attempt to give each data point its proper amount of influence over the parameter estimates.
A simple linear regression would not provide the best solution as bad data would negatively influence the ‘correct trend’ followed by the data. Therefore, weighting schemes may be used based on the source of data, simple linear regression statistics, or simple accordance of weighting based on visual verification. Thus in this way more precise coefficients may be obtained.

\[ F = \sum_{i=1}^{n} w_i (Y_i - \bar{Y})^2 \]  

(3.3)

Thus when applied to the least squares regression routine, the weighting is incorporated into the objective function such that the final matrix form accounts each point its own weighting. In Eqn. (3.3) above, the least squares error for each data point is multiplied by its pre-allocated weighting. Thus a data point with a lower weighting would not carry a significant “weight” in the least squares regression.

\[ A = (X^T W X)^{-1} X^T W y \]  

(3.4)

The main disadvantage to using this method is that the weightings are not exactly known and must be estimated. This may be done by visually assessing the data and specifying higher or lower weightings than a reference value of one for individual data points. An alternative is by undertaking a simple un-weighted regression and then using the standard error for each data point to calculate a weighting. However, this method may introduce random errors into the work due to the weighting being based upon a local fitting of the equation rather than a global fitting, and was not looked at in this work.
3.3.3. Fragmentation

Fragmentation is the breaking down of a chemical into its structural constituents, e.g. ethane with the formula C₂H₆ may be fragmented into two -CH₃ structural groups. It forms the basis for the group contribution concept in that an inadequate structural definition may cause a method to produce erroneous predictions.

Prior to the development of computers, group contribution methods were developed with all calculations being done by hand. Models were kept simple and were regressed to small datasets. Only a handful of simple structural groups were mostly employed to ensure that prediction methods were easy to use. However, with the advent of the computer, automated fragmentation routines and regression functions became the norm allowing for more functional groups to be regressed from larger training sets of data. Development of the current model utilised the automatic fragmentation software package developed by DDBST and implemented within their Artist program (Gmehling et al., 2009).

Fragmentation is undertaken based upon the definitions of the different functional and structural groups as stored within an “ink-file”. The groups are stored according to a specific priority. The priorities of the different structural and functional groups are determined by their definition. For example, an aldehyde (-CHO) could be fragmented by the –CH and =O groups, where the –CH and =O are fragments/groups on their own. Therefore, for the aldehyde to be recognised, it would require a higher fragmentation priority number than its two composite groups (the software will search for the higher priority –CHO group first before trying to find the lower priority –CH and =O groups). It is therefore important that a group which consists of smaller groups always has higher priority.

The definition of the structural groups is also important as they determine the type of bonds and atoms to which the bonds are made within a compound when fragmentation is undertaken. The group definition of an aldehyde group is stored within the ink-file with the following format:

<table>
<thead>
<tr>
<th>Line</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>Aldehyde in Chain§Aldeh§</td>
</tr>
<tr>
<td>(2)</td>
<td>3 2 59 59</td>
</tr>
<tr>
<td>(3)</td>
<td>C 2 2 K 0 Ja</td>
</tr>
<tr>
<td>(4)</td>
<td>O 1 1 K 0 Ja</td>
</tr>
<tr>
<td>(5)</td>
<td>C 4 1 * 0 Nein</td>
</tr>
<tr>
<td>(6)</td>
<td>1 2 2 K</td>
</tr>
<tr>
<td>(7)</td>
<td>1 3 1 K</td>
</tr>
</tbody>
</table>

Line (1) - The group is Aldehyde connected in a chain. The mnemonic abbreviation of the group name is given between the “§”-characters.

Line (2) - This line states that there are 3 atoms and 2 bonds. Next are the subgroup and main group number (in this case 59; the two separate numbers are needed for certain other methods e.g. UNIFAC)
Line (3)
C – First atom of the group is C
2 – C has a maximum of 2 neighbours
2 – C has a minimum of 2 neighbours
K – C is joined to the other atoms in the structural group via a chain (not ring) bond. K, N, R or A are used to represent chain, non-aromatic, ring or aromatic bonds respectively (a * is used when the type of atom and bond is irrelevant)
0 – C has no charge
Ja (German for ‘yes’) - after the group is found, mark this atom as found (a structure may be defined plus a required neighbourhood with the neighbourhood atoms being set to ‘Nein’ (German for ‘no’). The program will then find the main group and surrounding atoms (Ja and Nein atoms) but will only mark the Ja-atoms as part of the fragment)

Line (4) and (5) - see Line (3)

Line (6)
This line indicates the type of bonds between the different atoms states that atom 1 (in this case C) is connected to atom 2 (in this case O) by a double (2) bond which is part of a chain

Line (7) - see Line (6)

3.4. Summary

Experimental data used in the formulation of the model and regression of model parameters was obtained from the Dortmund Database (Gmehling et al., 2009). As the database consisted of a large amount of data collected from numerous journals in literature, rigorous filtration of the data was required. Filtration and correlation of data was undertaken using interfaces created through Microsoft Visual Basic with data management being performed with a Microsoft Access database. This increased the ease in which data may be accessed and manipulated.

Regression for equation parameters was undertaken using weighted linear regression to allow certain components with less reliable data to be provided with a lower weighting. Functional groups were defined as per fragmentation rules followed within the Dortmund Database Artist program. This allowed for easier regression of group contribution values for functional groups.
4. Development of the model

4.1. Model Development

From a statistical point of view, a good correlating equation fits the experimental data accurately obtaining statistically significant point value estimates of the coefficients. Represented graphically for liquid thermal conductivity for a simple organic compound, one would obtain a model such as that shown in Figure 4.1 below. A good equation may help compensate for random errors in experimental data and can produce a range of consistent values. However, if the experimental data is correlated to a more complex model than the trend followed by the data or the available theory describing the behaviour of the data, then experimental errors may be amplified in the usage of the model (interpolation and extrapolation of the data).

![Graph of liquid thermal conductivity vs. temperature for n-butane at 1atm](image)

**Figure 4.1: Liquid thermal conductivity vs. temperature for n-butane at 1atm [DDB (Gmehling et al., 2009)]**

A review of liquid thermal conductivity data for organic compounds indicated that the property decreases linearly with an increase in temperature from temperatures greater than the triple point up to the normal boiling point. After the normal boiling point the property follows, along the saturation curve, a trend similar to that of the property at an elevated pressure. Alcohols tend to deviate slightly from normal behaviour at lower temperatures close to the triple point.

However, glycols, which have multiple hydroxyl groups, follow a completely different trend as shown in Figure 4.3 and Figure 4.5 below. For ethylene glycol and polymers of it, the data deviates from the normal negative trend at a temperature of approximately 423 K. On the right side of this temperature, the data follows the normal negative linear trend of liquid thermal conductivity. The gradient of the
left hand side section of the graph decreases with an increase in the number of carbon atoms in the compound as shown in Figure 4.2.

![Graph showing slope of liquid thermal conductivity vs. temperature for ethylene glycols and its polymers vs. number of carbon atoms for the high and low temperature sections](image1)

**Figure 4.2: Slope of liquid thermal conductivity vs. temperature for ethylene glycols and its polymers vs. number of carbon atoms for the high and low temperature sections**

![Graph showing liquid thermal conductivity vs. temperature for diethylene glycol](image2)

**Figure 4.3: Liquid thermal conductivity vs. temperature for diethylene glycol (data from DDB (Gmehling et al., 2009))**

The curvature in the thermal conductivity vs. temperature plot of the smaller glycols is similar to that of water as shown in Figure 4.4. With the chemical formula of H₂O, water was sometimes considered to be the precedent to methanol in the alcohol family. However, in the absence of a carbon bond, the
oxygen atom in water forms two hydrogen bonds instead of the one normally present in an hydroxyl group. This causes the thermal conductivity of water to behave in the same way as the glycols. This leads one to assume that the hydrogen bond changes the way in which heat conduction occurs in associating liquids.

Figure 4.4: Liquid thermal conductivity vs. temperature for water (data from DDB (Gmehling et al., 2009))

Figure 4.5: Liquid thermal conductivity vs. temperature for pentaethylene glycol (data from DDB (Gmehling et al., 2009))

A naive but useful picture of this can be formulated from a description given by Palmer (1948) (Palmer, 1948). Hydrogen bonding within liquids were said to change the way in which heat was
conducted. Instead of conduction occurring only through the vibration and collisions of particles, heat was assumed to be conducted via the breaking and reforming of intra-molecular hydrogen bonds. The bonds were said to break at higher temperatures, taking up heat, and reforming at lower temperatures, giving up heat. The chains can be said to be oriented in the direction of heat flow with the bonds breaking at one end being replaced at the other. The temperature coefficient must be related in some way to this hydrogen bonding. At low temperatures, hydrogen bonds are rather stable thus breaking and reforming does not contribute significantly to thermal conductivity. With increasing temperature, the activation energy required to break hydrogen bonds is available and thermal conductivity increases. At higher temperatures, the number of hydrogen bonds is significantly reduced (equilibrium in the non-bonded state) and the thermal conductivity approaches that of normal components. This is due to the enthalpy and entropy of hydrogen bond formation being similar for all hydrogen bonding components. This switching to normal behaviour occurs at approximately the same temperature interval for the different components.

Therefore, the linear relationship between liquid thermal conductivity and temperature will be used to create a simple model for correlation of the experimental data:

$$\lambda = mT + c$$  \hspace{1cm} (4.1)

where, $m$ is the gradient and $c$ the intercept. The model will not be applicable to components that form two or more hydrogen bonds at lower temperatures.

Most correlation methods such as that of Lakshmi and Prasad (1987) (Lakshmi and Prasad, 1992) or Reidel (1951) (Reidel, 1951) utilize models based upon similar trends found in experimental data. However, the datasets utilised in obtaining these models were usually very small, being limited to literature available from public databases or sourced from other publishers, and may not have provided a large enough representation to identify specific behaviours of the different families. Another problem encountered, was the utilisation of too many parameters in some models. As the number of model parameters is increased, so does the accuracy of the regression and the fit of the correlating equation to the data. However, this results in further anomalies in the regression, such as inter-correlation between the model parameters. Inter-correlating parameters, in most cases, are deprived of any physical significance. This is a problem which must be strictly avoided. From the above points, the aim of this work is to create a simple model with a minimum number of parameters.

A comparison of the experimental data at pressures above and below 1.5 atm indicates that liquid thermal conductivity has a relatively weak dependency on pressure and that there are copious amounts of high pressure thermal conductivity data available in literature. This may indicate a need for high-pressure data within industry.

Another reason for this is the relatively high volatilities of some compounds. To obtain liquid thermal conductivity at saturation conditions, the property has to be measured under pressure to prevent a
phase change occurring during experimental work. After an isotherm, which clearly depicts the pressure trend followed by liquid thermal conductivity, is obtained, extrapolation for a data point at one atmosphere may be undertaken.

An evaluation of available experimental data indicated that up to moderately high pressures a linear relationship between liquid thermal conductivity and pressure is often observed, similar to that of liquid thermal conductivity and temperature. However, at higher pressures (in the region of 150 to 200 bar), a weak parabolic trend may be observed. As this is similar to the dependence of compressed liquid volume on pressure, thermal conductivity may depend linearly on the volume in this range.

Hence, based on the previous analyses of the experimental data, a simple model for thermal conductivity could take the form:

\[
\lambda(T, P) = \lambda(T_{\text{ref}}) \times f(T - T_{\text{ref}}) \times g(P - 101.3kPa)
\]  

(4.2)

As shown in Eqn. (4.2) an estimation method needs to consist of three parts, i.e. estimation of low-pressure thermal conductivity at an absolute or component dependent reduced reference temperature, a low-pressure thermal conductivity dependence on temperature, and a dependence of thermal conductivity on pressure as a function of temperature.

It was decided that developing a model representing both the temperature and pressure dependence would be too large a task for a master’s dissertation, thus only the temperature dependence was accounted for in this work. To represent the first two required parts for the model, the following linear equation was proposed based on the simple model of Eqn. (4.1):

\[
\lambda = \lambda_{\text{ref}} + A \times (T - T_{\text{ref}})
\]  

(4.3)

In Eqn. (4.3) \(\lambda_{\text{ref}}\), which is the equation intercept, is the thermal conductivity of the organic liquid at the reference temperature, and \(A\) is the gradient of the graph of thermal conductivity versus temperature. The next step was to select an appropriate reference temperature.

The reference temperature needs to have a physical relevance to the property being estimated. Therefore, the normal boiling point or the critical point temperature, or a standard temperature such as 298 K may be used. However, as shown previously at the critical point, thermal conductivity for all compounds diverges sharply from normal behaviour. Thus utilising the critical point as a reference temperature would not be appropriate as thermal conductivity diverges asymptotically as critical point conditions are approached.
Figure 4.6: Thermal conductivity (W.m$^{-1}$.K$^{-1}$) at the normal boiling point sorted into different bin ranges (375 components)

Figure 4.7: Thermal conductivity (W.m$^{-1}$.K$^{-1}$) at a standard temperature of 298 K sorted into different bin ranges (149 components)

From Figure 4.6 and Figure 4.7 above, it may be seen that thermal conductivity at the normal boiling point covers a much wider range than the thermal conductivity at a fixed standard temperature of 298 K. This wider range would help improve the temperature dependence within the model by providing a larger range of thermal conductivity values.

In addition the normal boiling point provides a corresponding state where the molecules have approximate identical chemical potential relative to the ideal gas state. And thermal conductivity data at the normal boiling temperature are available for a much larger number of components than at 298 K.

Based on the above arguments, the normal boiling point was selected for use as the reference temperature, resulting in the final model equation given below:
\[ \lambda = \frac{A}{T_B} \times \left(1 - \frac{T}{T_B}\right) + B \]  

(4.4)

In Eqn. (4.4) \( A \) is the slope of the model and \( B \) is the equation intercept or liquid thermal conductivity at the normal boiling point, and both constants should be compound specific. The equation may be used for correlating data for all organic compound families except glycols, for reasons as explained previously. It is not applicable to the first compounds of the different hydrocarbon families, viz. n-alkanes, n-alcohols, etc., such as methane or methanol as these compounds tend to deviate from the trend followed by the rest of the respective families as mentioned in Moller (2007) (Moller, 2007).

However, Eqn. (4.4) is not meant for use for data regression only. To create a prediction method, \( A \) and \( B \) were regressed to all the data in the training set and predictive equations for the two compound specific constants were formed using the group contribution concept. These predictive equations may then be used to calculate the constants for any organic compound within the range of applicability of the method.

### 4.2. The Group Contribution Concept

The property of a pure compound, according to the group contribution principle, may be calculated as the sum of the contributions of the different structural groups (e.g. \(-\text{CH}_2\), \(-\text{C}==\), \(-\text{OH}\), \(-\text{CONH}<\), \(-\text{CHOOH}\), etc.) of which it is composed assuming that the effects of the individual structural groups are additive (Moller, 2007).

Accordingly, the contribution scheme for the slope of the model is represented as:

\[ A = \sum_{i=0}^{k} n_i \Delta A_i \]  

(4.5)

In the above equation, the slope \( A \) is calculated using a linear combination of \( \Delta A_i \), the contribution of the individual structural groups towards the gradient for the compound, and \( n_i \), the frequency of the individual structural groups within the compound of interest. Accordingly, when the slope (\( A \)) is plotted against the number of carbons for the n-alkanes series, a linear trend is noted as shown in Figure 4.8. This provides verification that the assumed contribution scheme for calculation of the slope works properly.
In comparison with Eqn. (4.5), a contribution scheme need not be simple or linear. The following is an example of the non-linear contribution schemes proposed by Nannoolal et al. (2007) (Nannoolal et al., 2007):

$$C = \frac{M^d \sum v_i \Delta C_i + e}{n^a + b} + c$$  \hspace{1cm} (4.6)

Eqn. (4.6) takes into account the physical aspect of the structural contribution by use of the molecular weight, denoted by $M$ and the number of heavy atoms, denoted by $n$. The problem with a nonlinear model such as this is the large number of parameters that are sometimes used ($a$ to $e$).

A non-linear dependency was found to exist between the model intercept which is the thermal conductivity at the normal boiling point and the number of carbon atoms in the respective compounds. The trend displayed by the data could be interpreted in two ways. The first way was to assume that the data followed an exponential type trend, which may be linearized using an exponential function, as shown in Figure 4.9. The second possible interpretation was that the data followed two negative linear trends with a steeper slope for the first four compounds.

Application of the second interpretation would require two separate gradient constants being calculated. This would have resulted in a larger error in the use of the prediction method. Therefore, the first interpretation of an exponential function was used. It conveniently describes the steep change in the intercept for the smaller compounds in a family and the less sensitive change between the larger compounds.
Figure 4.9: Model intercept (B) vs. number of carbon atoms for the n-alkane series displaying a non-linear relationship

Hence, linearization of the trend was performed by initially utilizing a natural logarithm to smooth the data, and subsequently the number of heavy atoms within the compound of interest to linearize the expression. When the expression of \( \frac{(n^a) \times \ln(B)}{\ln(n^a)} \) was plotted against the number of carbon atoms in the molecule, a linear relationship was attained as show in Figure 4.10 below.

Figure 4.10: Linearized expression for model intercept (B) vs. number of carbon atoms for the n-alkane series displaying the linearized relationship

The expression was then used to develop a linearized contribution scheme for the calculation of the intercept \( B \). The resultant group contribution equation for prediction of the model intercept was:

\[
B = \exp \left( \frac{\ln(n^a)}{n^a} \times \sum_{i=0}^{m} \nu_i \Delta B_i \right) \quad (4.7)
\]
In the above equation, \( n' \) is the number of heavy atoms in the compound (count all atoms minus number of hydrogen atoms), \( v_i \) is the frequency of the individual structural groups, and \( \Delta B_i \) is the contribution of the individual structural groups within the compound of interest.

Application of the group contribution prediction schemes indicated that they worked reasonably well for most organic families. However, the exception was found to be the alcohol family. Application of the prediction schemes to the n-alcohol family produced fairly moderate predictions. However, when the results were plotted, as may be seen in Figure 4.11 below, the prediction models do not produce the correlated model values for the slope or the intercept correctly.

![Figure 4.11: Model slope (A) and intercept (B) vs. number of carbon atoms for the n-alcohol series without the size dependency term added](image)

Figure 4.11: Model slope (A) and intercept (B) vs. number of carbon atoms for the n-alcohol series without the size dependency term added

Figure 4.12 below shows the difference between the correlated and predicted slope values. One may see that this difference increases linearly with the number of carbon atoms in the compound. Moreover, a change in the trend between compounds with seven or less and eight or more carbon atom may be seen. When final regression was undertaken on a trial basis, the group contribution scheme did not regress accurately to the training set. Therefore, a correction was needed to represent the size dependency as indicated in Figure 4.12. Similar behaviour had been observed by Nannoolal (Nannoolal, 2006) and Moller (Moller, 2007) and led to the differentiation of alcohol groups on long and short chains.

The correction for the hydroxyl group representing the alcohols would depend upon the number of carbons within the compound as well as the frequency of the group. In addition, two hydroxyl groups were included in the model to account for the size dependence of the alcohols. The first was for use with compounds with seven or less carbon atoms, and the second for compounds with eight or more carbon atoms.
Previous work within the group found the size dependency to exist for associating compounds, such as the alcohols, amines and ketones, and the larger hydrocarbon families of alkanes and alkenes (Moller, 2007). However, within this work, it was found that the size dependence was negligible for most associating compounds with the only exception being the alcohols.

The modification of the group contribution schemes included the addition of two extra terms. The initial term takes into account the new size dependent structural contributions. The second term accounts for the size dependent constants. This was done in preference to a correction being included for the alcohols, as further modification of the model may be done at a later date if and when more data becomes available.

The final group contribution prediction schemes are as follows:

\[
A = \sum_{i=1}^{n} \nu_i \Delta A_i + n^c \times \sum_{j=1}^{m} \nu_j \Delta A_j + \sum_{k=1}^{n} \Delta A_k \]  \hspace{1cm} (4.8)

\[
B = \exp\left(\frac{\ln (n^c)}{n^a} \times \left(\sum_{i=1}^{n} \nu_i \Delta B_i + n^c \times \sum_{j=1}^{m} \nu_j \Delta B_j + \sum_{k=1}^{n} \Delta B_k\right)\right) \]  \hspace{1cm} (4.9)

In equations (4.8) and (4.9) above, the subscript

- \(i\) represents all size independent groups
- \(j\) represents the size dependent groups (viz. \(-\text{OH}\)) and
- \(k\) represents the size dependent group constants

The term \(n^c\) is included to account for the number of carbon atoms in the size dependency.
The application of the size dependency within the alcohol family accounts for the interaction between the hydroxyl group and its surroundings. Within smaller compounds the –OH group would have a larger effect on the surrounding atoms. However, as the size (number of atoms) of the compound increases, the –OH group would have a smaller and more negligible effect on the entire compound.

As may be seen in Figure 4.13 below, the size dependency terms improve the correlation between the model parameters and those predicted via the respective group contribution schemes.

![Figure 4.13: Model slope (A) and intercept (B) vs. number of carbon atoms for the n-alcohol series with the size dependency term added](chart.png)
5. Results and Discussion

The development of a simple correlating equation for a set of experimental data may be considered as a “curve fitting” exercise (Moller, 2007). However, after the data correlation is complete, creation of a prediction model is required for group contribution models. The regression of a group contribution type model to experimental data is not as simple as the correlation of experimental data to a single correlating equation. The regression process in this work required numerous steps in the validation of the experimental data and the different trends followed by the various organic families. Moreover, the validation of data was dependent upon the correlation of the data with the group contribution model equations. This was to ensure that the best and most correct fit to the data was obtained.

It is due to the above aspects in the development of a group contribution model, viz. data correlation of a single equation to various trends amongst various chemical families, that inaccuracies and unforeseen problems may appear when the model is complete. Similarly, there are numerous reasons for different results being obtained from the various models and equations for the prediction, interpolation and extrapolation of liquid thermal conductivity. A simple equation may not regress well to all the experimental data within a training set. However, it is the aim of a group contribution method to be able to provide accurate predictions for all the families contained within the training set.

Figure 5.1: Liquid thermal conductivity vs. temperature for heptane (Gmehling et al., 2009)

Another aspect that was considered was the temperature range of the experimental data being used. The properties of a compound close to the melting point and normal boiling point may differ from the
trends followed by the compound as a liquid, as may be seen in Figure 5.1 above. Below the normal boiling point the liquid property of a compound is determined at a reference pressure of one atmosphere. Above the normal boiling point, the compound must be considered along the saturation curve which exists at higher pressures so that liquid values may be obtained for the property.

As was mentioned previously under Data validation, data at the saturation curve were used where available in the development of the new model. The change in the slope, as seen in Figure 5.1 above, was assumed to contribute an insignificant percentage towards the overall relative mean deviation.

However, there is a limited amount of reliable experimental data available above the boiling point (Chemistry, 2012). With the experimental data from the DDB, the range of temperature for which reliable predictions may be made was increased to between reduced temperatures of approximately 0.3 to 0.8. However, within the training set many compounds had much smaller temperature ranges, often between reduced temperatures of approximately 0.4 and 0.7.

5.1. Hydrocarbon Compounds

Hydrocarbon compounds are the simplest of all the organic compounds, consisting of only two elements, namely carbon and hydrogen. They are the easiest family to represent using the group contribution approach and are thus used as the framework in the creation of most prediction methods. The simplest of the hydrocarbons are the n-alkanes, where each consecutive compound in the series has one extra CH₂ group than the previous compound. Consequently, if a property follows the group contribution scheme, the n-alkane family should follow a perfect trend that may be represented in a linear or linearized form as seen in Figure 5.2 below.

![Figure 5.2: Model slope (A) and intercept (B) vs. number of carbon atoms for the n-alkanes](image)

Moreover, if a method is able to predict the property of the n-alkanes and subsequently the n-alkene family accurately then the method displays potential of being applicable to the other hydrocarbon families and potentially all organic liquids.
A review of the model constants for the n-alkane series revealed that the larger compounds did not follow the expected trends very well. This may be attributed to much more data being available for compounds containing ten or less carbon atoms within the n-alkane series. This would result in the regression forcing the group contribution schemes to fit better to the compounds for which more data is available. In this case, this would be the smaller hydrocarbon compounds. Moreover, from the complete training set of 331 compounds, 267 have ten or fewer carbon atoms.

Therefore, higher errors arose mainly amongst the larger compounds in the series. Regression of the group contribution schemes found that the model constants $A$ and $B$ for the n-alkanes correlated accurately to the scheme equations (Eqns. (4.5) and (4.7)) and the results are shown in Table 5.1. The accuracy of the regression may be seen in Figure 5.3 below for tetradecane.

![Figure 5.3: Liquid thermal conductivity vs. temperature for tetradecane (data from the DDB (Gmehling et al., 2009))](image)

Subsequently, although there was limited data available for cyclic alkanes and numerous structural isomers, the model fitted the available experimental data fairly accurately.
Table 5.1: Relative mean deviation [%] of thermal conductivity estimation for the different families of hydrocarbons for the different models used.

<table>
<thead>
<tr>
<th>Group</th>
<th>Number of compounds</th>
<th>Proposed Method</th>
<th>Relative mean deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Proposed Method</td>
<td>ND</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td></td>
<td></td>
<td>88</td>
</tr>
<tr>
<td>Alkanes</td>
<td></td>
<td></td>
<td>47</td>
</tr>
<tr>
<td>Non-cyclic alkanes</td>
<td></td>
<td></td>
<td>36</td>
</tr>
<tr>
<td>Cyclic alkanes</td>
<td></td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>Alkenes</td>
<td></td>
<td></td>
<td>16</td>
</tr>
<tr>
<td>Non-cyclic alkenes</td>
<td></td>
<td></td>
<td>12</td>
</tr>
<tr>
<td>Cyclic alkenes</td>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>Aromatic hydrocarbons</td>
<td></td>
<td></td>
<td>25</td>
</tr>
</tbody>
</table>

Application of the method to the alkene family was limited as there were fairly few alkene compounds (16 compounds) as compared to alkane (47 compounds). However, compared to the prediction capability of previous methods, the current group contribution scheme allows much better correlation and prediction for the thermal conductivity of the alkene family.

No alkyne experimental data was found within literature. It was also evident from all other group contribution models for thermal conductivity that there was no experimental thermal conductivity data for alkyne components available for public or academic use. A search through other thermophysical property databases such as Beilstein (Beilstein, 2008), and ChemSpider (ChemSpider) also indicated no available alkyne data.

Application of the method to aromatic compounds consisted of the use of structural groups representing a double bonded carbon atom within an aromatic ring. This was consistent with the work from previous methods (Olivier, 2010, Moller, 2007). A review of experimental data for the aromatic hydrocarbons indicated that majority of the data consisted of structural isomers and data following arene substitution patterns. There was insufficient data available to allow development of a correction to account for isomers. However, there was a noted improvement in the prediction for aromatic compounds as compared to previous methods.
Table 5.2: Relative mean deviation [%] of liquid thermal conductivity prediction for hydrocarbon compounds. The number in superscript is the number of data points used; the main number is the RMD for the respective reduced temperature range.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3 – 0.4</td>
<td>2.35$^{108}$</td>
<td>7.06$^{98}$</td>
<td>6.74$^{105}$</td>
<td>5.88$^{108}$</td>
<td>6.27$^{108}$</td>
</tr>
<tr>
<td>0.4 - 0.5</td>
<td>2.30$^{95}$</td>
<td>5.32$^{64}$</td>
<td>4.96$^{74}$</td>
<td>8.09$^{95}$</td>
<td>10.35$^{695}$</td>
</tr>
<tr>
<td>0.5 - 0.6</td>
<td>2.54$^{1381}$</td>
<td>6.41$^{1340}$</td>
<td>4.79$^{1360}$</td>
<td>9.39$^{1378}$</td>
<td>10.55$^{1378}$</td>
</tr>
<tr>
<td>0.6 - 0.7</td>
<td>3.36$^{521}$</td>
<td>7.07$^{390}$</td>
<td>7.27$^{806}$</td>
<td>12.34$^{416}$</td>
<td>15.77$^{516}$</td>
</tr>
<tr>
<td>0.7 - 0.9</td>
<td>5.22$^{114}$</td>
<td>6.28$^{104}$</td>
<td>7.98$^{105}$</td>
<td>7.61$^{107}$</td>
<td>14.60$^{107}$</td>
</tr>
<tr>
<td>0.3 - 0.9</td>
<td>2.73$^{2819}$</td>
<td>6.28$^{2686}$</td>
<td>5.49$^{2750}$</td>
<td>9.41$^{2804}$</td>
<td>11.45$^{2804}$</td>
</tr>
</tbody>
</table>

As may be seen in Table 5.2, the majority of the data for the hydrocarbon compounds fell between the reduced temperatures of 0.4 to 0.7. The highest errors were found between the reduced temperatures of 0.7 to 0.9 as this was the range wherein data from along the saturated liquid curve was used. As mentioned earlier, the trend of the data along the saturation curve deviates slightly from that of the other data. It was seen that although the method of Sastri and Rao (Sastri and Rao, 1993) was developed to account for this deviation, the proposed method still achieved superior results.

5.1.1. Forcing Rules

It was found in previous work (Moller, 2007) that the contributions for the structural groups of -CH3, >CH2, >CH- and >C< for bonds within a hydrocarbon compound followed a linear trend when plotted against the molecular weight of the groups (as shown in Figure 5.4 below). This would be expected as there is a difference in one hydrogen atom between successive groups from the CH₃ down to the C atom.
Regression was undertaken using the respective group contribution schemes for the structural contributions. It was found that regression yielded trends for the hydrocarbon structural groups that deviated somewhat from the linear scheme. Forcing functions where therefore implemented to ensure a more linear fit and thus “physically realistic results”.

5.2. Oxygen compounds

Development of physical property prediction methods have always been more difficult for oxygenated compounds. This is especially true in the case of hydrogen bonding compounds. Since hydrogen bonding is stronger than other intermolecular forces in non-electrolytic liquids, more energy is required to dissociate intermolecular contacts.

As illustrated in Table 5.3, thermal conductivity at the normal boiling point drastically increases with an increase of the number of oxygen atoms within a compound. This increase also depends upon the type of bond the oxygen atoms are involved in (3-hexanone and 1-hexanol).

Table 5.3: Liquid thermal conductivity of hexane and 4 different oxygenated hexane compounds at their normal boiling points (Gmehling et al., 2009)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Thermal Conductivity (W.mol⁻¹.K⁻¹)</th>
<th>Number of Oxygen Bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexane</td>
<td>0.0996</td>
<td>0</td>
</tr>
<tr>
<td>3-Hexanone</td>
<td>0.1233</td>
<td>1 (Ketone)</td>
</tr>
<tr>
<td>1-Hexanol</td>
<td>0.1177</td>
<td>1 (Alcohol)</td>
</tr>
<tr>
<td>1,6-Hexanediol</td>
<td>0.1775</td>
<td>2 (Alcohol)</td>
</tr>
<tr>
<td>1,2,6-Hexanetriol</td>
<td>0.2314</td>
<td>3 (Alcohol)</td>
</tr>
</tbody>
</table>
These different types of inter-molecular bonding may be represented using different structural groups. However, temperature dependence of intra-molecular bonding is not representable using the model developed here and thus contributes to the errors between predicted values and experimental values.

Results for the oxygenated compounds and a comparison with the selected literature methods are presented in Table 5.4 below. As was expected, the deviations obtained for oxygenated compounds were higher than in case of the hydrocarbon compounds.

<table>
<thead>
<tr>
<th>Group</th>
<th>Number of compounds</th>
<th>Relative mean deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Proposed Method</td>
<td>ND</td>
</tr>
<tr>
<td>All Oxygenated Compounds</td>
<td>142</td>
<td>76</td>
</tr>
<tr>
<td>Carboxylic Acids</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Alcohols</td>
<td>27</td>
<td>24</td>
</tr>
<tr>
<td>Aromatic Alcohols</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Diols</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>Ethers</td>
<td>16</td>
<td>12</td>
</tr>
<tr>
<td>Esters</td>
<td>74</td>
<td>25</td>
</tr>
<tr>
<td>Ketones</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Aldehydes</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Non-Cyclic Carbonates</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

There was a vast improvement obtained for the prediction of ethers, esters and ketones as can be seen from a comparison of the relative mean deviations with older methods in Table 5.4. The prediction for carboxylic acids can be seen to be greatly improved as well; however, as only three compounds were available for regression to the group contribution model this does not provide a very good representation of the carboxylic acid family. A similar conclusion may be drawn for aldehydes and aromatic alcohols. Application of the method to aliphatic alcohols was fairly similar in accuracy as compared to the Sastri and Rao [1993] method (Sastri and Rao, 1993) (4.81 % compared to 4.96 % respectively).

Only one compound was available for regression of the group contribution value for non-cyclic carbonates. It was not possible to remove use of this structural group and allocate the compound to other structural groups as the carbonate structural group (-OCOO-) is one of the main groups as defined within previous work. Moreover, use of this group increases the applicability of the new
model, as the previous methods were unable to account for carbonates. The result was therefore accepted, however the result should be used with caution, even though a similar low value of the thermal conductivity was predicted using the Sato and Reidel method (Poling et al., 2004).

![Figure 5.5: Liquid thermal conductivity vs. reduced temperature for 1,2-Ethanediol [Data obtained from DDB (Gmehling et al., 2009)]](image)

In case of diols, ethanediol and propanediol were left out of the regression. This was done as the thermal conductivity for these two compounds exhibited an untypical temperature dependence (similar to that of water), as shown in Figure 5.5. Similarly, thermal conductivity of glycols could not be predicted as they follow a similar curvature as shown in Figure 4.3 under Model Development.

As seen in Table 5.5, the proposed method produced slightly higher deviations for the reduced temperature range of 0.7 to 0.9 for hydrocarbons. Although there were few data points available for the low temperature range of 0.4 to 0.5, the method produced greatly reduced prediction errors as compared to previous methods.

It should be noted that the group contribution methods are more often applied to the prediction of properties for larger and more complex compounds, for which no experimental data are available. These components are often not stable at higher reduced temperatures.
Table 5.5: Relative mean deviation (RMD) [%] of liquid thermal conductivity prediction for oxygenated compounds. The number in superscript is the number of data points used; the main number is the RMD for the respective reduced temperature range.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3 - 0.4</td>
<td>2.66$^{97}$</td>
<td>4.41$^7$</td>
<td>31.65$^{90}$</td>
<td>20.17$^{97}$</td>
<td>31.65$^{97}$</td>
</tr>
<tr>
<td>0.4 - 0.5</td>
<td>4.41$^{79}$</td>
<td>6.79$^{466}$</td>
<td>18.26$^{472}$</td>
<td>16.38$^{479}$</td>
<td>26.69$^{479}$</td>
</tr>
<tr>
<td>0.5 - 0.6</td>
<td>4.91$^{762}$</td>
<td>8.67$^{903}$</td>
<td>14.22$^{745}$</td>
<td>13.73$^{760}$</td>
<td>21.2$^{760}$</td>
</tr>
<tr>
<td>0.6 - 0.7</td>
<td>5.09$^{486}$</td>
<td>9.32$^{253}$</td>
<td>15.19$^{477}$</td>
<td>14.86$^{484}$</td>
<td>23.59$^{484}$</td>
</tr>
<tr>
<td>0.7 - 0.9</td>
<td>5.81$^{446}$</td>
<td>13.01$^{64}$</td>
<td>17.46$^{410}$</td>
<td>21.72$^{440}$</td>
<td>29.8$^{440}$</td>
</tr>
<tr>
<td>0.3 - 0.9</td>
<td>4.79$^{1970}$</td>
<td>8.78$^{93}$</td>
<td>16.51$^{924}$</td>
<td>15.55$^{1960}$</td>
<td>24.26$^{1960}$</td>
</tr>
</tbody>
</table>

5.3. Halogen compounds

Experimental data for fluorinated and chlorinated compounds were available largely for compounds containing less than five carbon atoms (50 % of the fluorine compounds and 79 % of the chlorine compounds). The number of structural groups used for these families were therefore kept to a minimum to allow more data per group and hence increase the reliability of the results. A large amount of this data consisted of multifunctional compounds. Instead of utilising group interaction terms to account for the effect of the different halogen groups on each other, structural groupings were used. These groupings differentiated between aromatic and non-aromatic carbon bonds, and between carbons with one or two other halogen atoms bonded to it and in this way accounted for the interactions between the different halogen groups (Moller et al., 2008).

The bromine data consisted primarily of mono-functional compounds with very few multi-functional compounds. Therefore, only two structural groups (bromine attached to aromatic carbon and bromine attached to non-aromatic carbon) as used by Moller et al. (Moller et al., 2008) were regressed for. Use of groups to account for multi-functional bonds was seen as unnecessary due to the lack of multifunctional compounds containing bromine.
Table 5.6: Relative mean deviation [%] of thermal conductivity estimation for the different families of halogenated compounds and the different models used.

<table>
<thead>
<tr>
<th>Group</th>
<th>Proposed Method</th>
<th>Number of compounds</th>
<th>Relative mean deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Proposed</td>
<td>ND</td>
<td>SRa</td>
</tr>
<tr>
<td>Halogenated Compounds</td>
<td>Method</td>
<td>Method</td>
<td></td>
</tr>
<tr>
<td>Fluorinated</td>
<td>ND</td>
<td>66</td>
<td>32</td>
</tr>
<tr>
<td>Chlorinated</td>
<td>SRa</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>Brominated</td>
<td>SRe</td>
<td>14</td>
<td>9</td>
</tr>
<tr>
<td>Iodinated</td>
<td>LP</td>
<td>11</td>
<td>6</td>
</tr>
</tbody>
</table>

Results for the different families of halogenated compounds are provided in Table 5.6. Only one functional group was used for iodinated compounds as there were only two compounds containing iodine within the training set. The data for the iodine compounds were obtained from four different sources dating as far back as 1965 and 1951 (Gmehling et al., 2009). As stated previously, data from as far back as this may not be accurate as the experimental equipment used was not of as high a standard as that available today. However, due to the lack of data, the compounds were kept for use. Results for the proposed method were better across the temperature range as opposed to other methods, as seen in Table 5.7 below, with a better overall RMD.

Table 5.7: Relative mean deviation (RMD) [%] of liquid thermal conductivity prediction for halogenated compounds. The number in superscript is the number of data points used; the main number is the RMD for the respective reduced temperature range.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3 - 0.4</td>
<td>8.9170</td>
<td>2.76^8</td>
<td>15.4^70</td>
<td>10.7^70</td>
<td>28.39^70</td>
</tr>
<tr>
<td>0.4 - 0.5</td>
<td>5.1^235</td>
<td>4.26^60</td>
<td>21.63^235</td>
<td>9.69^235</td>
<td>23.88^235</td>
</tr>
<tr>
<td>0.5 - 0.6</td>
<td>4.71^147</td>
<td>6.72^134</td>
<td>20.93^347</td>
<td>9.97^347</td>
<td>27.23^347</td>
</tr>
<tr>
<td>0.6 - 0.7</td>
<td>5.28^283</td>
<td>9.03^105</td>
<td>24.93^283</td>
<td>11.84^283</td>
<td>39.48^283</td>
</tr>
<tr>
<td>0.7 - 0.9</td>
<td>8.62^49</td>
<td>12.28^98</td>
<td>24.8^249</td>
<td>10.85^549</td>
<td>64.54^249</td>
</tr>
<tr>
<td>0.3 - 0.9</td>
<td>5.9g^1184</td>
<td>8.22^95</td>
<td>22.51^1184</td>
<td>10.5g^1184</td>
<td>37.41^1184</td>
</tr>
</tbody>
</table>

The regression results for halogenated compounds were superior to previous methods, with large improvements (greater than 30%) being obtained for fluorine, chlorine and bromine compounds. The main problem encountered was higher deviations for data at the low and high end of the temperature range. The higher deviation for the halogenated compounds as compared to the other families was attributed to the large amount of scatter within the data. Moreover, the available data, being mainly
from multifunctional compounds, resulted in higher errors being obtained for the model slopes as compared to the model intercept. A better account for the errors was shown when the halogen structural groups were plotted against their atomic radii and the trends checked.

5.3.1. **Group 17 Trends**

The halogen group atoms of fluorine, chlorine, bromine and iodine followed a similar trend to that of the hydrocarbon groups as shown in Figure 5.4. This trend is structurally related to the groups and therefore may be represented using the molecular weight, as was done for the hydrocarbon structural groups. However, as the halogen structural groups contain only one atom each it was noted that it would be more appropriate using the atomic radii of the compounds to represent the trend. The structural contributions were found to be inversely proportional to the atomic radii squared and are shown for the slope and intercept of the model equation in Figure 5.6 and Figure 5.8.

Figure 5.6 below shows that the group contribution values for the halogen atoms follow a linear trend when plotted against the respective structural group atomic radii squared. The atomic radius was used as a representation of the size of the respective atoms. However, it was found that fluorine did not follow the trend perfectly. This was explained by looking at the electronegativities of the halogens in Table 5.8.

![Figure 5.6: Model intercept (B) contribution vs. respective atomic radii squared for a halogen attached to a non-aromatic carbon (♦ - fitted group value)](image)

The Pauling electronegativities of chlorine, bromine and iodine increased linearly; however, the value for fluorine was slightly higher than the expected value if the trend followed by the lower three atoms of the family was extrapolated backwards. This phenomenon may be explained by looking at the electronic configuration of the halogen atoms.
Figure 5.7: Pauling electronegativities vs. atomic radii for the halogen atoms

Table 5.8: Electronic configuration for the first four halogen atoms from the periodic group 17

(Chemistry, 2012)

<table>
<thead>
<tr>
<th>Element</th>
<th>No. of electrons/shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine</td>
<td>2, 7</td>
</tr>
<tr>
<td>Chlorine</td>
<td>2, 8, 7</td>
</tr>
<tr>
<td>Bromine</td>
<td>2, 8, 18, 7</td>
</tr>
<tr>
<td>Iodine</td>
<td>2, 8, 18, 18, 7</td>
</tr>
</tbody>
</table>

Fluorine was shown to have the least amount of electrons in its orbitals and would thus form the smallest atom from the four halogens. It therefore has the highest electronegativity from the halogen groups. Although all the halogen compounds form hydrogen halides; fluorine is the only one that acts both as a hydrogen bond donor and acceptor. Possible hydrogen bond acceptors must exhibit small size and high electron density, such as fluorine, nitrogen and oxygen.

The above trends of Figure 5.6 and Figure 5.7 were therefore used for defining a set of forcing rules which the halogen structural groups within halogenated compounds must follow. Figure 5.8 shows that chlorine, which has data from 4 compounds behind the regression for its contribution, does not match the expected trend. Although fluorine with 6 compounds, bromine with 10 compounds and iodine with 2 compounds form a much better fit. Therefore, extrapolating from the straight line trend followed by the other halogen atoms, a new, more physically realistic value was calculated for chlorine. The results obtained from using this new value produced slightly higher errors, but a more physically realistic representation for chlorine would provide a much better prediction than a value regressed from one or two datasets which may or may not have been erroneous.
As mentioned previously, due to the small amount of experimental data being available to back up regression results, if the few data sets available contain “bad data”, this may render a method useless. Therefore, correlation techniques such as that used here for the halogen groups and previously for the hydrocarbon groups, may be applied to other families when there is little data available for regression of certain structural groups, for example, primary, secondary and tertiary amines or alcohols.

Figure 5.8: Model slope (A) contribution vs. respective atomic radii squared for a halogen attached to a non-aromatic carbon (♦ - fitted group value, ◊ - new group value)

Figure 5.9: Model intercept (B) contribution vs. respective atomic radii squared for a halogen attached to an aromatic carbon (♦ - fitted group value)
The only problem when utilising such a correlation technique when there is little or no data available, is the ability to test the results obtained. For example, regression for group 37 from Figure 5.10 above was done with only one available data set for the training set. With no test data, the accuracy of the result cannot be tested. After applying the linear fit as shown in Figure 5.10, the training set error for the data used for structural group regression increased, but so did the confidence in the contribution for group 37 as it has a physical relevance added to it. Deviations shown in Table 5.6 and Table 5.7 were calculated using the more physically realistic contributions.

5.4. Nitrogen compounds

Data for nitrogen containing compounds did not show any untypical trends and no modifications of the group contribution model were required. Ammonia has much weaker hydrogen bonding than water and the behaviour found for diols should be much less pronounced in the case of diamines (for which no data were available). There were data for fewer compounds available for regression of the structural contributions as compared to the other families. However, the method produced a much lower deviation as compared to previous methods as shown in Table 5.9. The method produces notably lower errors for all the reduced temperature ranges, as shown in Table 5.10, except the highest one of 0.7 to 0.9.

The method has greater applicability for nitrogen compounds (31 compounds) compared to other group contribution methods (23 compounds for Nagvekar and Daubert (Nagvekar and Daubert, 1987) being the highest). The only problem encountered was data available for only one compound for the regression of the 6-membered aromatic nitrogen ring structural group (group 88). Although the data utilized was obtained from a reliable reference, usage of the group should be done with caution as there is no way to validate the accuracy of the structural contribution. The structural group was
therefore included in the method so that it is available if required, and so that it may be recalculated at a later stage when more data becomes available.

Table 5.9: Relative mean deviation [ % ] of thermal conductivity estimation for the different families of nitrogen compounds and the different models used.

<table>
<thead>
<tr>
<th>Group</th>
<th>Number of compounds</th>
<th>Relative mean deviation ( % )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Proposed Method</td>
<td>ND</td>
</tr>
<tr>
<td>All nitrogen compounds</td>
<td>31</td>
<td>23</td>
</tr>
<tr>
<td>Amides</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Nitrates</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Amines</td>
<td>18</td>
<td>13</td>
</tr>
<tr>
<td>Primary amines</td>
<td>9</td>
<td>5</td>
</tr>
<tr>
<td>Secondary amines</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Tertiary amines</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>6-membered aromatic nitrogen rings</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Nitriles</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>Nitrites</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 5.10: Relative mean deviation (RMD) [%] of liquid thermal conductivity prediction for nitrogen compounds. The number in superscript is the number of data points used; the main number is the RMD for the respective reduced temperature range.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3 - 0.4</td>
<td>3.24^3</td>
<td>1.3^5</td>
<td>16.05^3</td>
<td>8.9^3</td>
<td>20.1^8</td>
</tr>
<tr>
<td>0.4 - 0.5</td>
<td>3.03^74</td>
<td>8.87^57</td>
<td>15.69^52</td>
<td>10.69^74</td>
<td>19.23^74</td>
</tr>
<tr>
<td>0.5 - 0.6</td>
<td>3.34^88</td>
<td>21.45^65</td>
<td>16.05^52</td>
<td>8.28^58</td>
<td>12.22^88</td>
</tr>
<tr>
<td>0.6 - 0.7</td>
<td>2.4^34</td>
<td>11.84^29</td>
<td>17.23^30</td>
<td>8.36^34</td>
<td>7.47^34</td>
</tr>
<tr>
<td>0.7 - 0.9</td>
<td>4.32^19</td>
<td>14.46^19</td>
<td>17.83^19</td>
<td>3.09^19</td>
<td>7.24^19</td>
</tr>
<tr>
<td>0.3 - 0.9</td>
<td>3.17^223</td>
<td>14.43^175</td>
<td>16.42^146</td>
<td>8.67^223</td>
<td>13.68^223</td>
</tr>
</tbody>
</table>

67
Results for the tertiary amines indicated that the method of Nagvekar and Daubert (Nagvekar and Daubert, 1987) provided a better prediction with a lower error. However, the higher deviations in case of the new method are accepted and recommendation is made for its use as the primary and secondary amines provided greatly improved results as compared to past methods. Moreover, as may be seen in Figure 5.11, when the three different amine structural groups were graphed against their respective radii squared, it was seen that the results follow a similar trend as displayed in Figure 5.4 for the hydrocarbon structural groups.

5.5. Other compounds

Table 5.11: Relative mean deviation [%] of thermal conductivity estimation for all other organic families and the different models used.

<table>
<thead>
<tr>
<th>Group</th>
<th>Number of compounds</th>
<th>Relative mean deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Proposed Method</td>
<td>ND</td>
</tr>
<tr>
<td>Sulphur Compounds</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Phosphates</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Metal Groups</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

As can be seen from the results in Table 5.11, there was extremely little experimental data available for regression of structural contributions for any other families. However, as the data is available, the structural groups are included in the method as they may not be covered by other group contribution methods. The results for these families should be used with extreme caution as there are minimal data backing them up.
The families of phosphates and the metal groups (stannane being the only one) produce similar results to that of the Sato and Reidel method (Poling et al., 2004), and this may thus provide a little confidence for the usage of these groups. The two sulphur compounds used were structural isomers, and thus produced a high error as the method cannot account for structural isomerism.

5.6. Testing the method

An indication of the versatility of the method cannot be derived from the results obtained utilizing the training set as this would just be an indication of the fit of the data by the model. To test how well the method actually works outside of the training set, a set of data external to the training set is required. The problem encountered when creating such a test set for thermal conductivity is the lack of experimental data external to that which was used to create the training set. Therefore, test data were obtained via two different methods.

The first way was by extrapolation of data at one atmosphere from compounds which had experimental data at pressures higher than one atmosphere only. This provided a test set of 65 compounds. However, a closer analysis of the data produced useable data for only a third of the compounds. To expand upon the test set, all the data which were excluded from the training set was reviewed. Compounds with three or more data points, which did not deviate too drastically when compared to results obtained from literature methods, were kept to be incorporated into a test set. The advantage of using these data is that it provides a larger test set with a wider range of data; the disadvantage is that these data were left out of the training set due to large scatter in the data or trends which did not match the respective family trends.

<table>
<thead>
<tr>
<th>Group</th>
<th>Number of compounds</th>
<th>Relative mean deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocarbons</td>
<td>10</td>
<td>Proposed Method ND SRa SRe LP</td>
</tr>
<tr>
<td>Halogen Compounds</td>
<td>4</td>
<td>12.97 16.44 4.33 15.62 60.33</td>
</tr>
<tr>
<td>Oxygen Compounds</td>
<td>20</td>
<td>6.68 26.40 12.76 11.70 17.22</td>
</tr>
<tr>
<td>Nitrogen Compounds</td>
<td>4</td>
<td>7.24 7.23 15.35 6.56 8.73</td>
</tr>
<tr>
<td>Overall</td>
<td>38</td>
<td>7.68 9.32 10.44 13.90 23.63</td>
</tr>
</tbody>
</table>

As shown in Table 5.12, utilisation of the test set indicates that the new method provides an improvement on previous methods, having a lower relative mean deviation of 7.68 % for a test set of
38 compounds which consisted of 328 data points. There is an indicated large improvement for prediction of oxygen-containing compounds with a relative mean deviation of 6.68 % compared to the lowest comparable value of 11.70 % for the method of Sato and Reidel (Poling et al., 2004). The halogen compounds exhibit the largest error for the test set. This could be attributed to the fact that the data were extrapolated from the pressure only data set. However, the halogens yield a much smaller error for the method of Sastri and Rao (Sastri and Rao, 1993).

Table 5.13: Relative mean deviation [%] of thermal conductivity estimation for the test set data for halogenated compounds and the different models used.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Proposed Method</th>
<th>SRa</th>
<th>ND</th>
<th>SRe</th>
<th>LP</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1-Dichloro-2,2,3,3,3-pentafluoropropane R225ca</td>
<td>10.08</td>
<td>2.81</td>
<td>20.09</td>
<td>17.62</td>
<td>49.70</td>
</tr>
<tr>
<td>1,3-Dichloro-1,1,2,2,3-pentafluoropropane R225cb</td>
<td>14.53</td>
<td>2.26</td>
<td>-</td>
<td>16.59</td>
<td>50.50</td>
</tr>
<tr>
<td>1,1,1,2,3,3,3-Heptafluoropropane [R227ea]</td>
<td>15.40</td>
<td>3.51</td>
<td>-</td>
<td>15.34</td>
<td>107.99</td>
</tr>
<tr>
<td>1,1,2-Trichloroethane</td>
<td>11.90</td>
<td>9.13</td>
<td>12.79</td>
<td>13.06</td>
<td>9.28</td>
</tr>
</tbody>
</table>

This result could be interpreted in two other ways. Looking at the prediction results in Table 5.13, one may assume that data for similar compounds was utilised by Sastri and Rao (Sastri and Rao, 1993) in their training set. Or that their training set contained a small amount of halogen compounds which followed the same trends as the test set compounds. According to the results of the training set, the current method produces a much better fit for halogenated compounds than that of Sastri and Rao (Sastri and Rao, 1993). Therefore, a larger test set would be required to provide a fuller picture of the shortcomings of the current method as compared to previous methods.

Similarly, a larger test set is required for the nitrogen compounds as the training set indicates a vast improvement as compared to previous methods.

5.7. Final results

The new method was regressed to a training set of 331 compounds consisting of 6282 data points. This was almost half of the initial 11000 data points available for modelling. Many of the data points were of low quality and had to be removed from the training set as mentioned earlier. As shown in Table 5.14 below, the training set produced an overall relative mean deviation of 3.87 % for the 331 compounds as compared to the lowest literature method of Nagvekar and Daubert (Nagvekar and Daubert, 1987) which produced a relative mean deviation of 7.03 % for 206 compounds.
Table 5.14: Relative mean deviation [%] of thermal conductivity estimation for the new method and literature methods.


<table>
<thead>
<tr>
<th>Group</th>
<th>Number of compounds</th>
<th>Proposed Method</th>
<th>Relative mean deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>ND</td>
<td>SRa</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>88</td>
<td>75</td>
<td>83</td>
</tr>
<tr>
<td>Oxygenated Compounds</td>
<td>142</td>
<td>76</td>
<td>138</td>
</tr>
<tr>
<td>Nitrogen Compounds</td>
<td>31</td>
<td>23</td>
<td>21</td>
</tr>
<tr>
<td>Halogenated Compounds</td>
<td>66</td>
<td>32</td>
<td>66</td>
</tr>
<tr>
<td>Sulphur Compounds</td>
<td>2</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Phosphates</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Metal Groups</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>All Compounds</td>
<td>331</td>
<td>206</td>
<td>310</td>
</tr>
</tbody>
</table>

The new method provides improved estimation of thermal conductivity behaviour for non-electrolyte organic liquids. It has a wider range of applicability than previous methods in that it covers a wider range of different components. The method uses 68 different first order structural groups which were regressed against the training set. However, some structural contributions were obtained from only one or two compounds. These structural groups should be used with caution as they were kept for use in the method to provide a greater applicability and a guide against which future models may be compared.

Table 5.15: Regression and prediction results for respective group contribution methods as reported in literature and calculated for the training set for the new model

<table>
<thead>
<tr>
<th>Method</th>
<th>Groups</th>
<th>Corrections</th>
<th>Reported in respective papers</th>
<th>Calculated from training set</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>NC</td>
<td>NP</td>
</tr>
<tr>
<td>Sastri &amp; Rao (1999)</td>
<td>32</td>
<td>7</td>
<td>208</td>
<td>748</td>
</tr>
<tr>
<td>Rodenbush et al. (1999)</td>
<td>84</td>
<td>10</td>
<td>228</td>
<td>1487</td>
</tr>
<tr>
<td>Sastri &amp; Rao (1993)</td>
<td>29</td>
<td>6</td>
<td>No results provided</td>
<td>310</td>
</tr>
<tr>
<td>Nagvekar &amp; Daubert</td>
<td>84</td>
<td>8</td>
<td>226</td>
<td>2089</td>
</tr>
<tr>
<td>Current Method</td>
<td>67</td>
<td>1</td>
<td>331</td>
<td>6282</td>
</tr>
</tbody>
</table>

Compared to previous methods, only the methods of Sastri and Rao (1993 and 1999) (Sastri and Rao, 1993, Sastri and Rao, 1999) utilized a small amount of structural groups for their method. This simplified approach can provide a good and simple prediction method for thermal conductivity.
predictions; however, when being applied to compounds with complicated and/or highly polar structures, the method may not be able to account for the different effects especially in case of atoms with higher electronegativities and may fail to provide an accurate prediction.

![Figure 5.12: Histogram representing the relative mean deviation [%] distribution for the new method compared to literature methods for training set data](image)

![Figure 5.13: Histogram representing the relative mean deviation [%] distribution for the new method compared to literature methods for test set data](image)
The new method which has been developed provides a large improvement over previous group contribution methods. As may be seen in Figure 5.12, the predicted deviations for over 90% of the training set fall below an error of 10%. And similarly in Figure 5.13, the predictive deviations for almost 70% of the test set fall below an error of 10%. The compounds for which higher errors were found are those which either consist of three or less carbons, or are structural isomers. The results for the test set were found to be lower than the training set, due to the type of data used as mentioned above. However the overall relative mean deviation for the test set was lower than the literature method.
6. Conclusions

Based on previous group contribution methods developed within our group, a more accurate and precise method with a better temperature dependency is presented for liquid thermal conductivity prediction. The model has a wider range of applicability than previous correlations and models, which were based on smaller experimental data sets.

The group contribution scheme accounts for size dependence for alcohols. This was not extended to other types of organic compounds such as ketones, carboxylic acids, etc., as there was insufficient data to model the respective behaviours. Linear forcing functions were incorporated into regression for the structural contributions to ensure the contributions correlated with structural behaviour.

The input requirements of the new method are the molecular structure, the normal boiling point, the number of heavy atoms (non-hydrogen) and the number of carbon atoms in the compound of interest.

The method produces a low overall relative mean deviation, with a much improved method for almost all of the families. Application of the method to a training set of 331 compounds (6264 data points) produced a relative mean deviation (RMD) of 3.87 %.

Applicability to data outside the training and performance of the model was tested using an external set of liquid thermal conductivity data. The RMD produced was 7.68 % for 38 compounds (328 data points). This error was found to be high as the test set contained data extrapolated from experimental data at elevated pressures, and other less reliable data which was excluded from the training set. From the results it may be concluded that the method may be applied to components outside the training set with reasonable confidence.
7. **Recommendations**

Evaluation of this project in conjunction to the continuation of the overall work of the group indicates the following requirements for future work to be undertaken:

- Development of a pressure dependence term for the proposed method may be undertaken;
- Experimental work should be undertaken to increase the amount of thermal conductivity data available for the chemical families which have data for less than five compounds;
- Use of the new experimental data should be made to improve upon the existing model and recalculate the values for structural contributions were too few compounds were used to calculate the group parameters in this work.
8. References


Chemistry, R. S. o. (2012), Rsc visual elements periodic table.


ThermTest-Inc. Thermtest - transient plane source - how it works. 2010 [cited Available from: http://www.thermtest.com/content/228455]


## Appendix A: Group Contribution Tables

### Aliphatic Carbon Groups

<table>
<thead>
<tr>
<th>Ink No.</th>
<th>Name</th>
<th>Description</th>
<th>Examples</th>
<th>Priority</th>
<th>ΔA</th>
<th>ΔB</th>
</tr>
</thead>
<tbody>
<tr>
<td>33 †</td>
<td>=C-C=</td>
<td>Conjugated double bonds (chain)</td>
<td>trans-1,3-Pentadiene</td>
<td>71</td>
<td>-8.434</td>
<td>0.2742</td>
</tr>
<tr>
<td>32 †</td>
<td>=C-C=</td>
<td>Conjugated double bonds (ring)</td>
<td>1,3-Cyclopentadiene</td>
<td>91</td>
<td>17.880</td>
<td>-2.5138</td>
</tr>
<tr>
<td>29</td>
<td>-CH3</td>
<td>Methyl group attached to a ring carbon</td>
<td>Methylcyclohexane</td>
<td>92</td>
<td>15.01</td>
<td>-2.813</td>
</tr>
<tr>
<td>26</td>
<td>CH2=</td>
<td>Double bonded carbon at the end of a chain/ring</td>
<td>1-Nonene</td>
<td>113</td>
<td>13.33</td>
<td>-2.164</td>
</tr>
<tr>
<td>27</td>
<td>-C=</td>
<td>Double bonded carbon in a chain with 2 carbon neighbours</td>
<td>2-Methyl-2-pentene</td>
<td>114</td>
<td>-10.10</td>
<td>1.201</td>
</tr>
<tr>
<td>24</td>
<td>-CH2-</td>
<td>CH2 in a ring attached to an electronegative atom</td>
<td>1,4-Dioxane</td>
<td>118</td>
<td>7.65</td>
<td>-1.860</td>
</tr>
<tr>
<td>15</td>
<td>&gt;C&lt;</td>
<td>C in a ring attached to an electronegative atom</td>
<td>Perfluorocyclopentane</td>
<td>119</td>
<td>-34.63</td>
<td>1.170</td>
</tr>
<tr>
<td>21</td>
<td>&gt;C=</td>
<td>Double bond between carbons in a ring</td>
<td>1,3-Cyclopentadiene</td>
<td>124</td>
<td>10.37</td>
<td>-1.217</td>
</tr>
<tr>
<td>12</td>
<td>&gt;C&lt;</td>
<td>C in a ring</td>
<td>1,1-Dimethylcyclopetane</td>
<td>128</td>
<td>-39.11</td>
<td>2.764</td>
</tr>
<tr>
<td>14</td>
<td>&gt;CH-</td>
<td>CH in a ring attached to an electronegative atom</td>
<td>Cyclopentanol</td>
<td>131</td>
<td>-14.43</td>
<td>-0.288</td>
</tr>
<tr>
<td>4</td>
<td>-CH2-</td>
<td>CH2 in a chain</td>
<td>n-Butane</td>
<td>136</td>
<td>2.33</td>
<td>-0.636</td>
</tr>
<tr>
<td>5</td>
<td>&gt;CH-</td>
<td>CH in a chain</td>
<td>3-Ethylpentane</td>
<td>137</td>
<td>-16.18</td>
<td>1.095</td>
</tr>
<tr>
<td>6</td>
<td>&gt;C&lt;</td>
<td>C in a chain</td>
<td>2,2,4-Trimethylpentane</td>
<td>138</td>
<td>-34.82</td>
<td>2.756</td>
</tr>
<tr>
<td>10</td>
<td>-CH2-</td>
<td>CH2 in a ring</td>
<td>Cyclohexane</td>
<td>139</td>
<td>4.67</td>
<td>-1.218</td>
</tr>
<tr>
<td>11</td>
<td>&gt;CH-</td>
<td>CH in a ring</td>
<td>Methylcyclohexane</td>
<td>140</td>
<td>-9.75</td>
<td>0.547</td>
</tr>
<tr>
<td>1</td>
<td>-CH3</td>
<td>Methyl group attached to a non-electronegative atom</td>
<td>2,2-Dimethylbutane</td>
<td>141</td>
<td>16.16</td>
<td>-2.589</td>
</tr>
<tr>
<td>20</td>
<td>=C-</td>
<td>Double bonded carbon in a chain with only 1 carbon neighbour</td>
<td>2-Heptene</td>
<td>142</td>
<td>4.83</td>
<td>-1.096</td>
</tr>
<tr>
<td>7</td>
<td>-CH2-</td>
<td>CH2 in a chain attached to an electronegative atom</td>
<td>Ethylenediamine</td>
<td>143</td>
<td>-3.94</td>
<td>-0.919</td>
</tr>
<tr>
<td>2</td>
<td>-CH3</td>
<td>Methyl group attached to an electronegative atom</td>
<td>N-Methylaniline</td>
<td>144</td>
<td>14.42</td>
<td>-2.754</td>
</tr>
<tr>
<td>8</td>
<td>-CH&lt;</td>
<td>CH in a chain attached to an electronegative atom</td>
<td>5-Ethyl-2-nonanol</td>
<td>145</td>
<td>-20.36</td>
<td>0.818</td>
</tr>
<tr>
<td>9</td>
<td>&gt;C&lt;</td>
<td>C in a chain attached to an electronegative atom</td>
<td>tert-Butanol</td>
<td>147</td>
<td>-37.15</td>
<td>1.966</td>
</tr>
<tr>
<td>Ink No.</td>
<td>Name</td>
<td>Description</td>
<td>Examples</td>
<td>Priority</td>
<td>∆A</td>
<td>∆B</td>
</tr>
<tr>
<td>--------</td>
<td>---------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>-------------------------------</td>
<td>----------</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aromatic Carbon Groups</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>-CH(a)&lt;</td>
<td>CH in an aromatic ring</td>
<td>Benzene</td>
<td>116</td>
<td>6.17</td>
<td>-1.220</td>
</tr>
<tr>
<td>17</td>
<td>&gt;C(a)&lt;</td>
<td>C in an aromatic ring</td>
<td>Propylbenzene</td>
<td>121</td>
<td>-11.00</td>
<td>0.726</td>
</tr>
<tr>
<td>18</td>
<td>&gt;C(a)&lt;</td>
<td>C in an aromatic ring attached to an electronegative atom</td>
<td>Aniline</td>
<td>123</td>
<td>-12.04</td>
<td>0.322</td>
</tr>
<tr>
<td>19</td>
<td>=C(a)&lt;</td>
<td>Aromatic carbon attached to three aromatic neighbours</td>
<td>Naphthalene</td>
<td>125</td>
<td>-6.19</td>
<td>-0.086</td>
</tr>
<tr>
<td>3</td>
<td>-CH3</td>
<td>Methyl group attached to an aromatic atom</td>
<td>1-Methyl naphthalene</td>
<td>146</td>
<td>17.40</td>
<td>-2.637</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>Halogen Groups</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>F-C-1Halo</td>
<td>Fluorine attached to a carbon with one other halogen atom</td>
<td>Perfluorocyclopentane</td>
<td>61</td>
<td>19.057</td>
<td>-2.1214</td>
</tr>
<tr>
<td>43</td>
<td>Cl-C-1Halo</td>
<td>Chlorine attached to a carbon with one other halogen atom</td>
<td>2-Bromo-2-chloro-1,1,1-trifluoroethane</td>
<td>65</td>
<td>21.743</td>
<td>-2.4678</td>
</tr>
<tr>
<td>149</td>
<td>Cl-C(=1 Halo)</td>
<td>Chlorine attached to a double bonded carbon with one other halogen atom</td>
<td>Tetrachloroethylene</td>
<td>66</td>
<td>14.202</td>
<td>-2.6812</td>
</tr>
<tr>
<td>44</td>
<td>Cl-C-2Halo</td>
<td>Chlorine attached to a carbon with two other halogen atoms</td>
<td>1,1,1-Trichloroethane [R140a]</td>
<td>67</td>
<td>16.272</td>
<td>-2.4102</td>
</tr>
<tr>
<td>40</td>
<td>Cl-</td>
<td>Chlorine attached to a non-aromatic carbon</td>
<td>Chloroethane</td>
<td>70</td>
<td>16.852</td>
<td>-2.2692</td>
</tr>
<tr>
<td>41</td>
<td>Cl-C(a)</td>
<td>Chlorine attached to an aromatic carbon</td>
<td>Chlorobenzene</td>
<td>76</td>
<td>20.216</td>
<td>-2.5325</td>
</tr>
<tr>
<td>42</td>
<td>Cl-C=</td>
<td>Chlorine attached to a double bonded carbon</td>
<td>2-Chloro-1,3-butadiene</td>
<td>77</td>
<td>23.059</td>
<td>-1.9803</td>
</tr>
<tr>
<td>35</td>
<td>F-</td>
<td>Fluorine attached to a non-aromatic carbon</td>
<td>1-Fluoropentane</td>
<td>78</td>
<td>28.679</td>
<td>-1.4986</td>
</tr>
<tr>
<td>37</td>
<td>F-C(a)</td>
<td>Fluorine attached to an aromatic carbon</td>
<td>Fluorobenzene</td>
<td>79</td>
<td>31.255</td>
<td>-2.2799</td>
</tr>
<tr>
<td>39</td>
<td>F-C-2Halo</td>
<td>Fluorine attached to a carbon with two other halogen atoms</td>
<td>1,1,1,2-Tetrachloro-2,2-difluoroethane [R112a]</td>
<td>93</td>
<td>14.832</td>
<td>-2.3602</td>
</tr>
<tr>
<td>47 †</td>
<td>I-</td>
<td>Iodine attached to carbon</td>
<td>Ethyl iodide</td>
<td>94</td>
<td>1.147</td>
<td>-3.3472</td>
</tr>
<tr>
<td>46</td>
<td>Br-C(a)</td>
<td>Bromine attached to an aromatic carbon</td>
<td>Bromobenzene</td>
<td>132</td>
<td>12.348</td>
<td>-2.9920</td>
</tr>
<tr>
<td>145</td>
<td>Br-C-2Halo</td>
<td>Bromine attached to a carbon with two other halogen atoms</td>
<td>Tribromomethane [R20B3]</td>
<td>133</td>
<td>13.232</td>
<td>-2.7571</td>
</tr>
<tr>
<td>45</td>
<td>Br-</td>
<td>Bromine attached to a non-aromatic carbon</td>
<td>1,2-Dibromoethane</td>
<td>135</td>
<td>6.135</td>
<td>-2.7263</td>
</tr>
<tr>
<td>Ink No.</td>
<td>Name</td>
<td>Description</td>
<td>Examples</td>
<td>Priority</td>
<td>∆A</td>
<td>∆B</td>
</tr>
<tr>
<td>--------</td>
<td>---------------</td>
<td>-------------------------------------------------------</td>
<td>---------------------------------------</td>
<td>----------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>61 †</td>
<td>O=C(-O-)2</td>
<td>Carbonate diester</td>
<td>Carbonic acid dimethyl ester</td>
<td>8</td>
<td>25.492</td>
<td>-1.1897</td>
</tr>
<tr>
<td>49*</td>
<td>-OH (n=&lt;7)</td>
<td>OH Group attached to a small molecule (n =&lt; 7)</td>
<td>2-Methyl-hexanol</td>
<td>21</td>
<td>2.150</td>
<td>-0.1041</td>
</tr>
<tr>
<td>50 †</td>
<td>C(a)-OH</td>
<td>Aromatic OH</td>
<td>2-Naphthol</td>
<td>22</td>
<td>-4.051</td>
<td>-1.5286</td>
</tr>
<tr>
<td>72</td>
<td>-CONH&lt;</td>
<td>Amide with two substituents attached to the nitrogen</td>
<td>N,N-Dimethylformamide (DMF)</td>
<td>25</td>
<td>11.442</td>
<td>0.8726</td>
</tr>
<tr>
<td>58</td>
<td>&gt;C=O</td>
<td>Ketone</td>
<td>Acetone</td>
<td>60</td>
<td>0.546</td>
<td>-0.2229</td>
</tr>
<tr>
<td>153*</td>
<td>-OH (n&gt;7)</td>
<td>OH Group attached to a large molecule (n &gt; 7)</td>
<td>5-Ethyl-2-nonanol</td>
<td>62</td>
<td>3.074</td>
<td>-0.1443</td>
</tr>
<tr>
<td>175**</td>
<td>-OH (n=&lt;7)</td>
<td>Short OH group constant (n=&lt;7)</td>
<td>2-Methyl-hexanol</td>
<td>64</td>
<td>7.450</td>
<td>-1.0202</td>
</tr>
<tr>
<td>48</td>
<td>C(a)-COOH</td>
<td>Aromatic COOH</td>
<td>Benzoic acid</td>
<td>74</td>
<td>13.727</td>
<td>-3.1523</td>
</tr>
<tr>
<td>66</td>
<td>-OCOO-</td>
<td>Carbonates O-C=O &amp; -O</td>
<td>Propylene carbonate</td>
<td>81</td>
<td>18.249</td>
<td>-2.0575</td>
</tr>
<tr>
<td>70</td>
<td>-CONH&lt;</td>
<td>Amide with no substituents</td>
<td>Acetamide</td>
<td>96</td>
<td>26.620</td>
<td>-3.0101</td>
</tr>
<tr>
<td>52</td>
<td>-O-</td>
<td>Aromatic oxygen</td>
<td>Furan</td>
<td>97</td>
<td>12.776</td>
<td>-1.4955</td>
</tr>
<tr>
<td>51</td>
<td>-O-</td>
<td>Ether oxygen</td>
<td>Diethyl ether</td>
<td>98</td>
<td>7.507</td>
<td>0.3052</td>
</tr>
<tr>
<td>55</td>
<td>-COO-</td>
<td>Formic acid ester</td>
<td>Formic acid ethyl ester</td>
<td>99</td>
<td>23.158</td>
<td>-2.8564</td>
</tr>
<tr>
<td>59</td>
<td>-CHO</td>
<td>Aldehyde in Chain</td>
<td>Acetaldehyde</td>
<td>101</td>
<td>12.744</td>
<td>-2.4582</td>
</tr>
<tr>
<td>53</td>
<td>-COOH</td>
<td>Carboxylic acid Group</td>
<td>Pentanoic acid</td>
<td>102</td>
<td>4.982</td>
<td>-1.6203</td>
</tr>
<tr>
<td>54</td>
<td>-COO-</td>
<td>Ester in a chain</td>
<td>1,3-Benzenedicarboxylic acid dimethyl ester</td>
<td>104</td>
<td>6.527</td>
<td>-1.0405</td>
</tr>
<tr>
<td>Ink No.</td>
<td>Name</td>
<td>Description</td>
<td>Examples</td>
<td>Priority</td>
<td>ΔA</td>
<td>ΔB</td>
</tr>
<tr>
<td>--------</td>
<td>--------</td>
<td>--------------------------------------------------</td>
<td>-------------------</td>
<td>----------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>89</td>
<td>-CtN</td>
<td>CN group attached to a carbon</td>
<td>Acetonitrile</td>
<td>11</td>
<td>25.543</td>
<td>-2.6877</td>
</tr>
<tr>
<td>93</td>
<td>-NH-</td>
<td>Secondary amines (ring) attached to carbon</td>
<td>Morpholine</td>
<td>12</td>
<td>9.092</td>
<td>0.5287</td>
</tr>
<tr>
<td>82</td>
<td>-NH-</td>
<td>Secondary amines (chain) attached to a carbon</td>
<td>Dibutylamine</td>
<td>15</td>
<td>9.835</td>
<td>0.3294</td>
</tr>
<tr>
<td>75</td>
<td>NO2-</td>
<td>Nitro group attached to a non-aromatic carbon</td>
<td>Nitromethane</td>
<td>26</td>
<td>28.361</td>
<td>-3.1016</td>
</tr>
<tr>
<td>76</td>
<td>NO2-</td>
<td>Nitro group attached to an aromatic carbon</td>
<td>Nitrobenzene</td>
<td>28</td>
<td>29.557</td>
<td>-3.4053</td>
</tr>
<tr>
<td>88 †</td>
<td>=N</td>
<td>Aromatic nitrogen in a six-membered ring</td>
<td>2-Methylpyridine</td>
<td>29</td>
<td>22.279</td>
<td>-0.8005</td>
</tr>
<tr>
<td>84</td>
<td>-N&lt;</td>
<td>Tertiary amine attached to carbon</td>
<td>N,N-dimethylaniline</td>
<td>36</td>
<td>-12.576</td>
<td>1.1656</td>
</tr>
<tr>
<td>81</td>
<td>NH2-</td>
<td>Primary amine attached to an aromatic carbon</td>
<td>Aniline</td>
<td>57</td>
<td>75.000</td>
<td>-2.2536</td>
</tr>
<tr>
<td>80</td>
<td>NH2-</td>
<td>Primary amine attached to a non-aromatic carbon</td>
<td>Ethylenediamine</td>
<td>59</td>
<td>5.175</td>
<td>-0.9976</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Other Groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>95 †</td>
</tr>
<tr>
<td>110 †</td>
</tr>
<tr>
<td>100 †</td>
</tr>
</tbody>
</table>

* indicates size dependency

** indicates a constant

† Group contribution value must be used with caution as there is minimal experimental data behind this value
Appendix B: Sample Calculations

Compound: 2-Ethylhexanol-2-ene

Number of carbon atoms: 8
Number of heavy atoms: 9
Normal Boiling Point: 464.4 K
Temperature: 323.15 K

<table>
<thead>
<tr>
<th>Group</th>
<th>Atoms</th>
<th>Frequency</th>
<th>(\Delta A)</th>
<th>(\Delta B)</th>
<th>OH Correction</th>
<th>(\Delta A) Total</th>
<th>(\Delta B) Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,9</td>
<td>2</td>
<td>16.161</td>
<td>-2.589</td>
<td>N</td>
<td>32.323</td>
<td>-5.177</td>
</tr>
<tr>
<td>4</td>
<td>2,3,8</td>
<td>3</td>
<td>2.330</td>
<td>-0.636</td>
<td>N</td>
<td>6.990</td>
<td>-1.907</td>
</tr>
<tr>
<td>7</td>
<td>6</td>
<td>1</td>
<td>-3.938</td>
<td>-0.919</td>
<td>N</td>
<td>-3.938</td>
<td>-0.919</td>
</tr>
<tr>
<td>20</td>
<td>4</td>
<td>1</td>
<td>4.832</td>
<td>-1.096</td>
<td>N</td>
<td>4.832</td>
<td>-1.096</td>
</tr>
<tr>
<td>27</td>
<td>5</td>
<td>1</td>
<td>-10.103</td>
<td>1.201</td>
<td>N</td>
<td>-10.103</td>
<td>1.201</td>
</tr>
<tr>
<td>153</td>
<td>7</td>
<td>8 *</td>
<td>3.074</td>
<td>-0.144</td>
<td>Y</td>
<td>24.593</td>
<td>-1.155</td>
</tr>
</tbody>
</table>

\[
\lambda = \frac{A}{T_B} \times (1 - \frac{T}{T_B}) + B
\]
\[
B = \exp\left(\frac{\ln(9)}{9} \times [-9.054]\right)
\]
\[
B = 0.1097 \text{ W.m}^{-1}\text{.K}^{-1}
\]

\[
\lambda = \frac{54.697}{464.4} \times (1 - \frac{323.15}{464.4} + 0.1097)
\]
\[
\lambda = 0.145 \text{ W.m}^{-1}\text{.K}^{-1}
\]

Calculated thermal conductivity: 0.145 W.m\(^{-1}\).K\(^{-1}\)
Experimental thermal conductivity: 0.143 W.m\(^{-1}\).K\(^{-1}\)
Error = \left\| \frac{0.145 - 0.143}{0.143} \right\| \times 100 = 1.74\%

* NB: Frequency of the alcohol group is multiplied by the number of carbon atoms in the compound
Compound: 1,2-Dibromo-1-chloro-1,2,2-trifluoroethane (Freon 113B2)

Number of carbon atoms: 2
Number of heavy atoms: 8
Normal Boiling Point: 366.02K
Temperature: 323.15K

<table>
<thead>
<tr>
<th>Group</th>
<th>Atoms</th>
<th>Frequency</th>
<th>ΔA</th>
<th>ΔB</th>
<th>OH Correction</th>
<th>ΔA Total</th>
<th>ΔB Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>2,5</td>
<td>2</td>
<td>-37.15</td>
<td>1.97</td>
<td>N</td>
<td>-74.30</td>
<td>3.93</td>
</tr>
<tr>
<td>39</td>
<td>3,7,8</td>
<td>3</td>
<td>14.83</td>
<td>-2.36</td>
<td>N</td>
<td>44.50</td>
<td>-7.08</td>
</tr>
<tr>
<td>44</td>
<td>4</td>
<td>1</td>
<td>16.27</td>
<td>-2.41</td>
<td>N</td>
<td>16.27</td>
<td>-2.41</td>
</tr>
<tr>
<td>145</td>
<td>1,6</td>
<td>2</td>
<td>13.23</td>
<td>-2.76</td>
<td>N</td>
<td>26.46</td>
<td>-5.51</td>
</tr>
</tbody>
</table>

\[ B = \exp\left(\frac{\ln(8)}{8} \times [-11.07]\right) \]

\[ B = 0.0562 \ W.m^{-1}.K^{-1} \]

\[ \lambda = \frac{A}{T_B} \times \left(1 - \frac{T}{T_B}\right) + B \]

\[ \lambda = \frac{12.93}{366} \times \left(1 - \frac{323.15}{366}\right) + (0.0562) \]

\[ \lambda = 0.0604 \ W.m^{-1}.K^{-1} \]

Calculated thermal conductivity: 0.0604 W.m\(^{-1}\).K\(^{-1}\)
Experimental thermal conductivity: 0.0676 W.m\(^{-1}\).K\(^{-1}\)

\[ \text{Error} = \left| \frac{0.0676 - 0.0604}{0.0604} \right| \times 100 = 10.71\% \]
Compound: Ethylbenzene

Number of carbon atoms: 8
Number of heavy atoms: 8
Normal Boiling Point: 409.3K
Temperature: 353.15K

\[
\lambda = \frac{A}{T_B^2} \times (1 - \frac{T}{T_B}) + B
\]

\[
B = \exp \left( \frac{\ln(8)}{8} \right) \times [-8.06]
\]

\[
B = 0.107 \, \text{W.m}^{-1}.\text{K}^{-1}
\]

Calculated thermal conductivity: \(0.1198 \, \text{W.m}^{-1}.\text{K}^{-1}\)
Experimental thermal conductivity: \(0.1175 \, \text{W.m}^{-1}.\text{K}^{-1}\)

\[
\text{Error} = \left| \frac{0.1175 - 0.1198}{0.1198} \right| \times 100 = 1.98\%
\]
**Compound: 1,3-Cyclopentadiene**

Number of carbon atoms: 5

Number of heavy atoms: 5

Normal Boiling Point: 313.8K

Temperature: 283.15K

<table>
<thead>
<tr>
<th>Group</th>
<th>Atoms</th>
<th>Frequency</th>
<th>∆A</th>
<th>∆B</th>
<th>OH Correction</th>
<th>∆A Total</th>
<th>∆B Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1</td>
<td>1</td>
<td>4.67</td>
<td>-1.218</td>
<td>N</td>
<td>4.67</td>
<td>-1.22</td>
</tr>
<tr>
<td>21</td>
<td>2, 5</td>
<td>2</td>
<td>10.37</td>
<td>-1.217</td>
<td>N</td>
<td>20.74</td>
<td>-2.43</td>
</tr>
<tr>
<td>32</td>
<td>3 &amp; 4</td>
<td>1</td>
<td>17.88</td>
<td>-2.514</td>
<td>N</td>
<td>17.88</td>
<td>-2.51</td>
</tr>
</tbody>
</table>

\[ B = \exp\left(\frac{\ln(5)}{5} \times [-6.17]\right) \]

\[ B = 0.1374 \text{ W.m}^{-1}.\text{K}^{-1} \]

\[ \lambda = \frac{A}{T_B} \times \left(1 - \frac{T}{T_B}\right) + B \]

\[ \lambda = \frac{43.29}{313.8} \times \left(1 - \frac{283.15}{313.8}\right) + (0.1374) \]

\[ \lambda = 0.1509 \text{ W.m}^{-1}.\text{K}^{-1} \]

Calculated thermal conductivity: 0.1509 W.m\(^{-1}\).K\(^{-1}\)

Experimental thermal conductivity: 0.1465 W.m\(^{-1}\).K\(^{-1}\)

Error = \left| \frac{0.1465 - 0.1509}{0.1509} \right| \times 100 = 3.00\%
**Compound: Naphthalene**

Number of carbon atoms: 10

Number of heavy atoms: 10

Normal Boiling Point: 491.3K

Temperature: 438.83K

![Naphthalene molecule](image)

<table>
<thead>
<tr>
<th>Group</th>
<th>Atoms</th>
<th>Frequency</th>
<th>∆A</th>
<th>∆B</th>
<th>OH Correction</th>
<th>∆A Total</th>
<th>∆B Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>2,3,4,5,7,8,9,10</td>
<td>8</td>
<td>6.17</td>
<td>-1.220</td>
<td>N</td>
<td>49.36</td>
<td>-9.76</td>
</tr>
<tr>
<td>19</td>
<td>1,6</td>
<td>2</td>
<td>-6.19</td>
<td>-0.086</td>
<td>N</td>
<td>-12.38</td>
<td>-0.17</td>
</tr>
</tbody>
</table>

\[
B = \exp \left( \frac{\ln(10)}{10} \times [-9.93] \right)

\[
\lambda = \frac{A}{T_B} \times (1 - \frac{T}{T_B}) + B

\]

\[
B = 0.1016 \text{ W.m}^{-1}.\text{K}^{-1}

\[
\lambda = \frac{36.98}{491.3} \times (1 - \frac{438.83}{491.3}) + (0.1016)

\[
\lambda = 0.1096 \text{ W.m}^{-1}.\text{K}^{-1}

\]

Calculated thermal conductivity: 0.1096 W.m\(^{-1}\).K\(^{-1}\)

Experimental thermal conductivity: 0.1121 W.m\(^{-1}\).K\(^{-1}\)

Error = \left| \frac{0.1121 - 0.1096}{0.1096} \right| \times 100 = 2.21\%
**Compound: Biphenyl**

Number of carbon atoms: 12

Number of heavy atoms: 12

Normal Boiling Point: 529K

Temperature: 472.65K

```
\begin{array}{cccccc}
\text{Group} & \text{Atoms} & \text{Frequency} & \Delta A & \Delta B & \text{OH Correction} & \Delta A \text{ Total} & \Delta B \text{ Total} \\
16 & 3 \text{ to } 12 & 10 & 6.17 & -1.220 & N & 61.70 & -12.20 \\
17 & 1.2 & 2 & -11.00 & 0.726 & N & -22.00 & 1.45 \\
\hline
\end{array}
```

\[
B = \exp\left(\frac{\ln(12)}{12} \times [-10.75]\right)
\]

\[
B = 0.1080 \text{ W.m}^{-1}.\text{K}^{-1}
\]

\[
\lambda = \frac{A}{T_B} \times (1 - \frac{T}{T_B}) + B
\]

\[
\lambda = \frac{39.70}{529} \times (1 - \frac{472.65}{529}) + (0.1080)
\]

\[
\lambda = 0.1166 \text{ W.m}^{-1}.\text{K}^{-1}
\]

Calculated thermal conductivity: \(0.1166 \text{ W.m}^{-1}.\text{K}^{-1}\)

Experimental thermal conductivity: \(0.1193 \text{ W.m}^{-1}.\text{K}^{-1}\)

\[
\text{Error} = \left(\frac{0.1193 - 0.1166}{0.1166}\right) \times 100 = 2.26\%
\]
Compound: 2-propanol

Number of carbon atoms: 3

Number of heavy atoms: 4

Normal Boiling Point: 355.5K

Temperature: 303.15K

\[
B = \exp \left( \frac{\ln(4)}{4} \times [-5.69] \right)
\]

\[
\lambda = \frac{A}{T_B} \times (1 - \frac{T}{T_B}) + B
\]

\[
\lambda = \frac{25.86}{355.5} \times (1 - \frac{303.15}{355.5}) + (0.1391)
\]

\[
\lambda = 0.1468 \text{ W.m}^{-1}.\text{K}^{-1}
\]

Calculated thermal conductivity: 0.1468 W.m\(^{-1}\).K\(^{-1}\)

Experimental thermal conductivity: 0.1396 W.m\(^{-1}\).K\(^{-1}\)

\[
\text{Error} = \left| \frac{0.1396 - 0.1468}{0.1468} \right| \times 100 = 5.16\%
\]

* NB: Frequency of the alcohol group is multiplied by the number of carbon atoms in the compound
Appendix C: Example Calculation Using the Mathias et al. Model

All equations used are obtained from the paper of Mathias et al. (Mathias et al., 2002) unless stated otherwise.

**General Definitions**

\[
\begin{align*}
\text{kmol} & := 1000 \text{mol} \\
\text{mPa} & := 0.001 \text{Pa} \\
\text{kPa} & := 1000 \text{Pa} \\
\text{dm} & := 0.1 \text{m}
\end{align*}
\]

\[
\begin{align*}
R & := 8.314 \frac{\text{J}}{\text{mol} \times \text{K}} \\
\mu \text{Pa} & := 10^{-6} \text{Pa}
\end{align*}
\]

**System Conditions \((T, P)\)**

\[
\begin{align*}
T & := 298.15 \text{K} \\
P & := 101.3 \text{kPa}
\end{align*}
\]

**Physical Property Parameters**

Example Component: n-Hexane

\[
\begin{align*}
M & := 86.177 \frac{\text{kg}}{\text{kmol}} \\
T_c & := 507.40 \text{K} \\
V_c & := 370.0 \frac{\text{cm}^3}{\text{mol}} \\
\omega & := 0.2975 \\
P_c & := 3014.419 \text{kPa}
\end{align*}
\]

Reference Component: Methane

\[
\begin{align*}
M_O & := 16.043 \frac{\text{kg}}{\text{kmol}} \\
T_{co} & := 190.60 \text{K} \\
V_{co} & := 99.0 \frac{\text{cm}^3}{\text{mol}} \\
\omega_o & := 0.01 \\
P_{co} & := 4600.155 \text{kPa}
\end{align*}
\]

**Critical density calculated from critical volume:**

\[
\rho_{co} := \frac{M_O}{V_{co}}
\]

\[
\rho_{co} = 0.162 \text{ kg} \times \text{dm}^{-3}
\]

**Calculation of viscosity and ideal gas heat capacity:**

Parameters fitted to data obtained from the DDB (Gmehling et al., 2009).

Viscosity calculated from DIPPR 102 (Gmehling et al., 2009) equation for vapour viscosity.
Ideal heat capacity calculated using polynomial form.

\[ \eta(T) := \frac{4.2769 \times 10^{-5} \times \left( \frac{T}{K} \right)^{0.88713}}{1 + \frac{1.445 \times 10^{-5}}{T} + \frac{1.834 \times 10^{-10}}{T^2}} \text{ mPa s} \]

\[ \lambda_{\text{int}}(T) := \frac{\eta(T)}{M} \times f_{\text{int}} \times \left( C_{\text{p id}}(T) - \frac{5 \times R}{2} \right) \]

\[ T_R(T) := \frac{T}{T_c} \]

\[ \eta(T) = 6.671 \times 10^{-3} \text{ mPa s} \]

\[ C_{\text{p id}}(T) = 144.469 \text{ J/} \text{molK} \]

\[ T_R(T) = 0.5876 \]

Density

The density was obtained using the BRW EoS as done by Ely and Hanley (Ely and Hanley, 1981). This was coded within VBA and density calculated at the required system conditions.

\[ \rho(T, P) := 0.1207068 \text{ kg/dm}^3 \]

Calculation of the Background Contribution

Internal degrees of freedom contribution was calculated from the modified Eucken correlation for polyatomic gases as given by Ely and Hanley (Ely and Hanley, 1983):

\[ \lambda_{\text{int}}(T) := \frac{\eta(T)}{M} \times f_{\text{int}} \times \left( C_{\text{p id}}(T) - \frac{5 \times R}{2} \right) \]

In the above equation,

\[ f_{\text{int}} := 1.3 \]

\[ \eta - \text{the viscosity of the dilute gas in the limit of zero density} \]

\[ \lambda_{\text{int}}(T) = 0.0126 \text{ W/mK} \]
Translation Contribution - Dimensionless Scaling Factor

Calculation of the empirical shape factors:

Coefficients for calculating the shape factors not available for n-hexane from Table 3 (pg 992, Mathias et al. (Mathias et al., 2002)) therefore they have to be calculated using equations 19 to 24 from the paper, which were correlated to shape factors calculated from available data. The six equations are presented below.

\[ \begin{align*}
\theta_{\lambda 1} & := (\omega - \omega_0) \times 0.59 \\
\theta_{\lambda 2} & := (\omega - \omega_0) \times 0.4 \\\n\theta_{\lambda 3} & := 0 \\
\phi_{\lambda 1} & := (\omega - \omega_0) \times 0.94 \\
\phi_{\lambda 2} & := (\omega - \omega_0) \times (-0.18) \\
\phi_{\lambda 3} & := 0
\end{align*} \]

The shape factors are then calculated using equations 15 and 16 from the paper of Mathias et al. (Mathias et al., 2002).

\[ \begin{align*}
\theta_{\lambda}(T) & := 1 + \theta_{\lambda 1} + \theta_{\lambda 2} \times \ln(T_R(T)) + \theta_{\lambda 3} \times \left(1 - \frac{1}{T_R(T)}\right) \\
\phi_{\lambda}(T) & := 1 + \phi_{\lambda 1} + \phi_{\lambda 2} \times \ln(T_R(T)) + \phi_{\lambda 3} \times \left(1 - \frac{1}{T_R(T)}\right)
\end{align*} \]

\[ \begin{align*}
\theta_{\lambda}(T) & = 1.1053 \\
\phi_{\lambda}(T) & = 1.2988
\end{align*} \]

A problem noted from the results is that the second shape factor, highlighted above, is not close to unity as it should be as n-hexane is a simple straight chain hydrocarbon with nothing to account for a high deviation from an ideal situation. This could be due to a deviation of the calculated shape factor constants from what they would be when regressed to experimental data.

Calculation of equivalent substance reducing factors:

The equivalent reducing factors where then calculated from equations 13 and 14.

\[ \begin{align*}
h_{\lambda}(T) & := \frac{V_c}{V_{co}} \times \phi_{\lambda}(T) \\
f_{\lambda}(T) & := \frac{T_c}{T_{co}} \times \theta_{\lambda}(T)
\end{align*} \]

\[ \begin{align*}
h_{\lambda}(T) & = 4.854 \\
f_{\lambda}(T) & = 2.943
\end{align*} \]
Calculation of dimensionless scaling factor:

This was calculated from equation 7. The scaling factor thus gives the deviation of the reference fluid from the compound of interest.

\[
F_{\lambda}(T) := \left( \frac{M_0}{M} \right)^{\frac{1}{2}} \times f_\lambda(T) \times h_\lambda(T) \times \frac{-2}{3}
\]

\[F_{\lambda}(T) = 0.2582\]

Translation Contribution - Reference Contribution

The reference contribution was calculated using the method of Ely and Hanley (Ely and Hanley, 1983). All equations for the calculation of the reference contribution were taken from the paper of Ely and Hanley (Ely and Hanley, 1983) unless stated otherwise.

The equivalent reducing factors are used to calculate the reference density and temperature for use in calculating the reference contribution.

\[\rho_0(T,P) := \rho(T,P) \times h_\lambda(T)\]

\[\rho_0(T,P) = 0.58591 \text{ kg dm}^{-3}\]

\[T_0(T) := \frac{T}{f_\lambda(T)}\]

\[T_0(T) = 101.324 \text{ K}\]

Coefficients for the three parts of the reference contribution:

Coefficient B is obtained from the FORTRAN example (Assael et al., 1998) as the B values from the Ely and Hanley paper gave results which were wrong.
Calculating the high density contribution:

\[
\exp_{\text{part}}(T, P) := \left[ A_3 + \frac{A_4}{T_{o}(T)^{3/2}} \right] \times \left[ \frac{\rho_{o}(T, P)}{\text{kg/dm}^3} \right]^{0.1} \\
+ \left( \frac{\rho_{o}(T, P)}{\rho_{co}} - 1 \right) \times \left( \frac{\rho_{o}(T, P)}{\text{kg/dm}^3} \right)^{0.5} \times \left[ A_5 + \frac{A_6}{T_{o}(T)/K} + \frac{A_7}{(T_{o}(T)/K)^2} \right]
\]

\[
\Delta \lambda_{o}(T, P) := \exp \left( A_1 + \frac{A_2}{T_{o}(T)/K} \right) \times \left[ (\exp(\exp_{\text{part}}(T, P))) - 1 \right] \times \frac{W}{\text{m} \times \text{K}} \times 10^{-3}
\]

\[
\Delta \lambda_{o}(T, P) = 0.6546 \frac{W}{\text{m} \times \text{K}}
\]

It was noted that when calculating the high density contribution using the equations provided by Ely and Hanley, the result obtained was too low. After comparison with the example obtained from a textbook by Assael et al. (Assael et al., 1998) it was noted that the equation provided a result that was of by a factor of a thousand. To correct for this, the factor of 10^{-3} was introduced into the equation.

### 8.1.1. Calculating the first density correction:

\[
\lambda_{\Omega}(T) := \left[ B_1 + B_2 \times \left( B_3 - \ln \left( \frac{T_{o}(T)/K}{B_4} \right) \right)^2 \right] \times \frac{W}{\text{m} \times \text{K}}
\]

\[
\lambda_{\Omega}(T) = 6.3077 \times 10^{-4} \frac{W}{\text{m} \times \text{K}}
\]

### 8.1.2. Calculating the dilute gas contribution:

\[
\eta_{o}(T) := \sum_{n=1}^{9} C_n \times \left( \frac{T_{o}(T)/K}{3} \right)^{n-4} \times 10^{-7} \times \text{Pa} \times \text{s}
\]

Firstly the dilute gas viscosity had to be calculated. A factor of 10^{-7} was used as per the example from Assael et al. (Assael et al., 1998).
Once the viscosity is obtained, the dilute gas contribution is calculated.

\[
\lambda_\varphi(T) := \frac{15 \times R}{4 \times M_o} \times \eta_o(T)
\]

\[
\lambda_\varphi(T) = 7.8154 \times 10^{-3} \frac{W}{m \times K}
\]

**Calculating the reference contribution:**

\[
\lambda_\varphi(T) = 7.8154 \times 10^{-3} \frac{W}{m \times K}
\]

\[
\lambda_\Omega(T) \times \frac{\rho_o(T,P)}{\text{kg/dm}^3} = 3.6958 \times 10^{-4} \frac{W}{m \times K}
\]

\[
\Delta \lambda_{\varphi}(T,P) = 0.6546 \frac{W}{m \times K}
\]

\[
\lambda_o(T,P) := \lambda_\varphi(T) + \lambda_\Omega(T) \times \frac{\rho_o(T,P)}{\text{kg/dm}^3} + \Delta \lambda_{\varphi}(T,P)
\]

\[
\lambda_o(T,P) = 0.6628 \frac{W}{m \times K}
\]

**Calculating the translational contribution:**

\[
\lambda_{\text{trans}}(T,P) := \lambda_o(T,P) \times F_{\lambda}(T)
\]

\[
F_{\lambda}(T) = 0.2582
\]

\[
\lambda_o(T,P) = 0.6628 \frac{W}{m \times K}
\]

\[
\lambda_{\text{trans}}(T,P) = 0.171 \frac{W}{m \times K}
\]

**Background Term**

\[
\lambda_{\text{bg}}(T,P) := \lambda_{\text{trans}}(T,P) + \lambda_{\text{int}}(T)
\]

\[
\lambda_{\text{bg}}(T,P) = 0.1837 \frac{W}{m \times K}
\]

\[
\eta_o(T) = 4.0216 \times 10^{-6} \text{ Pa} \times \text{s}
\]
Thermal Conductivity Prediction Results from Artist (DDB 2009 (Gmehling et al., 2009)) at 298.15K

<table>
<thead>
<tr>
<th>Method</th>
<th>Result</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nagvekar/Daubert</td>
<td>0.1231</td>
<td>W. m⁻¹.K⁻¹</td>
</tr>
<tr>
<td>Sastry/Rao</td>
<td>0.1168</td>
<td>W. m⁻¹.K⁻¹</td>
</tr>
<tr>
<td>Lakshmi</td>
<td>0.1366</td>
<td>W. m⁻¹.K⁻¹</td>
</tr>
<tr>
<td>Mathias et al.</td>
<td>0.1837</td>
<td>W. m⁻¹.K⁻¹</td>
</tr>
</tbody>
</table>

Experimental Thermal Conductivity (DDBST (Gmehling et al., 2009)): 0.1168 W. m⁻¹.K⁻¹

As may be seen from the sample calculation above, application of the predictive method of Mathias et al. requires an extremely long calculation but thus not provide highly accurate results. The method was applied to the training set of 331 compounds used for this work and yielded a relative mean deviation (RMD) of 297% for 202 compounds.

Table C-1: Relative mean deviation (RMD) of thermal conductivity prediction results for Mathias et al. (Mathias et al., 2002) (NC = number of compounds)

<table>
<thead>
<tr>
<th>Group Name</th>
<th>NC</th>
<th>RMD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocarbons</td>
<td>80</td>
<td>275.84</td>
</tr>
<tr>
<td>Oxygenated Compounds</td>
<td>73</td>
<td>477.57</td>
</tr>
<tr>
<td>Halogenated Compounds</td>
<td>47</td>
<td>62.00</td>
</tr>
<tr>
<td>All Sulphur Compounds</td>
<td>2</td>
<td>76.73</td>
</tr>
</tbody>
</table>

When the deviations’ for all the compounds to which the method was applied was sorted into different temperature groups, a noticeable trend was found. The RMD decreased as the reduced temperature increased. This suggested that the method works better at higher temperatures closer to or at the critical temperature. However, such a temperature range was not considered in this work.

Table C-2: Relative mean deviation (RMD) of thermal conductivity prediction results for Mathias et al. (Mathias et al., 2002) (ND = number of data points)

<table>
<thead>
<tr>
<th>Reduced Temperature</th>
<th>ND</th>
<th>RMD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3 - 0.4</td>
<td>175</td>
<td>453.74</td>
</tr>
<tr>
<td>0.4 - 0.5</td>
<td>1078</td>
<td>633.53</td>
</tr>
<tr>
<td>0.5 - 0.6</td>
<td>2121</td>
<td>199.56</td>
</tr>
<tr>
<td>0.6 - 0.7</td>
<td>997</td>
<td>80.66</td>
</tr>
<tr>
<td>0.7 - 0.9</td>
<td>382</td>
<td>19.56</td>
</tr>
</tbody>
</table>
Appendix D: Data Validation and Regression Interfaces

Figure D-1: Initial data validation interface
Figure D-2: Data validation interface including a correlation functions to validate trends
Figure D.3: Structural parameter contribution regression interface
Figure D-4: Data validation interface utilizing correlation of high pressure data.