

A New Group Contribution Method For The Estimation Of Thermal Conductivity For Non-Electrolyte Organic Compounds

Onellan Govender¹, Jürgen Rarey^{1,2,3,*}, Bruce C. Moller¹, Deresh Ramjugernath¹

¹ Thermodynamics Research Unit, School of Chemical Engineering, University of Kwa-Zulu Natal, Durban 4041, RSA

² DDBST GmbH, Marie-Curie-Str. 10, 26129 Oldenburg, Germany

³ Industrial Chemistry, Carl von Ossietzky University Oldenburg, 26111 Oldenburg, Germany

*Corresponding Author: E-mail: rarey@ddbst.de; Tel: +494417983846; Fax: +494417983330

Abstract

Optimum design of heat and mass transfer equipment form an integral part of cost-effective plant design. For this purpose, reasonably accurate data on thermal conductivity is required for all phases. During the determination of thermal conductivity of fluid phases, convective heat transport has to be strictly avoided. Modern reliable equipment is now available for the routine measurement of liquid thermal conductivity but due to the large amount of data needed and the costs of experiments, alternative sources such as predictive methods are often employed. Substantial effort has been invested into the development of models for prediction or correlation of liquid thermal conductivity. Prediction of liquid thermal conductivity based only 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, whereby the property is calculated using contributions of the different structural groups within the compound. Group contribution methods still have the potential to produce more reliable results than other approaches.

Methods for the estimation of the normal boiling point (Rarey and Cordes 2002 and Nannoolal *et al.* 2004), critical property data (Nannoolal *et al.* 2007), vapour pressures (Nannoolal *et al.* 2008 and Moller *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 under development for liquid thermal conductivity prediction. The data used to formulate the method will be obtained from the extensive Dortmund Data Bank (DDB) (Gmehling *et al.* 2007), which contains approximately 110000 thermal conductivity data points for almost 900 different compounds. The model should therefore have a wider range of applicability than previous correlations and models, which were based on a smaller set of experimental data.

Keywords: Thermal conductivity, group contribution, prediction

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:

$$J_q = -\lambda \nabla T \quad (1)$$

In the above equation, λ is the thermal conductivity; J_q is the heat flux and ∇T is the temperature

gradient. 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 (λ constant with respect to x), Equation 1 may then be integrated producing the following analogous equation for one-dimension heat conduction:

$$\dot{q}\Delta x = \lambda\Delta T \quad (2)$$

, where Δx is the shortest distance between two parallel layers inside the homogeneous phase and ΔT 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:

$$\lambda = \frac{\Delta Q\Delta x}{\Delta t A \Delta T} \quad (3)$$

, where ΔQ is the amount of heat transferred in the time interval Δt through an area with cross section A . In this equation, λ is a material constant, that depends on temperature and pressure (density) and the kind of material (pure component or mixture) itself.

Liquid Thermal Conductivity as a Function of Temperature and Pressure

According to Assael *et al.* (1998), any transport property, for example, thermal conductivity, may be written in terms of the state variables temperature and density, or molar volume, (as pressure is considered to be of “no direct importance” by the authors) as a function of three contributions:

$$\lambda(\rho_n, T) = \lambda_o(T) + \Delta\lambda(\rho_n, T) + \Delta\lambda_c(\rho_n, T) \quad (4)$$

The three contributions of equation (4) represent the dilute-gas contribution, the excess contribution and the critical enhancement contribution towards the thermal conductivity (Assael *et al.* 1998). The sum of the first two contributions is called the background contribution and represents the contribution of the liquid. It is the term often predicted for transport properties.

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 $\left(\frac{\partial P}{\partial V}\right)_T$ approaches zero. 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. This phenomenon is known as “critical enhancement” and is observed in pure components but not on mixtures.

Therefore, although thermal conductivity may be implicitly or explicitly dependent upon many different transport properties, according to Equation (3) and (4), the implicit temperature dependence requires that when deriving a predictive model, a correct temperature dependence be of high importance. A review of experimental data indicates that pressure dependent data are very common and that thermal conductivity has a weak dependency upon pressure at low to medium pressures and diverges closer to the critical point due to the aforementioned critical enhancement.

Data Correlation Models

When developing a method for prediction of a thermophysical property the first step is to select an equation, which can fit experimental data sufficiently well without employing an excessive amount of variables or input parameters. Millat *et al.* (2005) suggests that for a direct fit to

thermal conductivity data the following relationship is sufficient:

$$\lambda = A + BT + CT^2 \quad (5)$$

, 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 or solid-liquid saturation line. For the accurate representation of pure component thermal conductivity, data equations, which contain both temperature and pressure, are used (Nemzer *et al.* 1996).

It would be preferable to employ a function $\lambda(T,P)$ instead of $\lambda(T,V)$ as the latter would require knowledge of the density as a function of temperature and pressure in most practical applications. Up to moderately high pressures, a linear relationship between λ and P is often observed. A simple equation to model $\lambda(T,P)$ for liquids for example, could therefore be

$$\lambda(T, P) = (A + BT + CT^2) \times ([D + ET] \times [P - P^s]) \quad (6)$$

While expressions like this are applicable over a wide temperature and pressure range, they lead to large errors in the vicinity of the vapour-liquid critical point due to critical enhancement. In this work, no modelling or prediction of critical enhancement is currently under development and data in the vicinity of the critical point will not be included in the parameter regression.

Predictive Models

The previous section introduced ways for representing the behaviour of thermal conductivity data, which may not always be available. 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 in the following sections. Predictive methods may be split up into four main categories:

1. General correlation methods – these methods are typically based on one or more pure component properties. Typical properties used by these methods are molar mass, liquid density, heat capacity at constant pressure, heat of vaporization or the normal boiling point. As these methods shall 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 (1992). The book covers all methods for thermal conductivity predictions from the initial study by Weber in 1880 up to those by Herrick & Lielmezs and Kerr in 1985.
2. 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 would be 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.
3. Group contribution methods – these methods are similar to the family methods but are much more widely applicable if the groups are well defined. Model parameters are fitted to the groups, which make up the compounds.
4. Corresponding states methods – The theory of corresponding states, as given by Van der Waal (Smith *et al.* 2005), 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". Corresponding states methods are especially popular for hydrocarbons but are very often not applicable to the more complex compounds with sufficient reliability.

The empirical model by Sato and Riedel (1977), which required the temperature, critical temperature, and molecular weight for prediction of thermal conductivity of any organic compound, was found by Horvath 1992 to be the best general correlation. A simpler correlation by Lakshmi and Prasad (1992), based on the reference substance approach, only requires the temperature and molecular weight as input. 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 is also able to describe the critical enhancement contribution for pure fluids.

Group Contribution Methods Available In Literature

Nagvekar and Daubert (1987)

The method was one of the first group contribution methods created for predicting thermal conductivity. It was based upon the second order contribution scheme as set out by Benson and Buss (1958), which was based upon "nearest neighbour interactions". The temperature dependent equation of Reidel (1951) (Horvath 1992) was used as a basis for their group contribution model.

$$\lambda = A \left[1 + \frac{20}{3} (1 - T_r)^{2/3} \right] \quad (7)$$

In the above equation, λ 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:

$$\lambda = A + B(1 - T_r)^{2/3} \quad (8)$$

where A and B, are the group contribution parameters. A total of 84 groups and 8 group corrections were used. The method is only applicable within a temperature range of $0.3 < T_r < 0.9$.

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. Contrary to other methods, the normal boiling point temperature was used as a reference instead of the critical temperature.

The model used was based on experimental data for 37 organic liquids by Miller (1976). Two separate relationships were noted, with the behaviour of the liquids being different above and below the liquid boiling point. The model is as follows:

$$\lambda = \lambda_B (T_B/T)^{0.5}, \quad T \leq T_B \quad (9)$$

$$\lambda = \lambda_B (T_B/T)^{1.15}, \quad T \geq T_B \quad (10)$$

Here, λ_B is the thermal conductivity at the normal boiling point and is calculated using group contributions. The exponent values 0.5 and 1.15 are regressed values constant for all liquids below and above the boiling points respectively. The method consists of 29 groups and 6 group corrections.

Rodenbush, Viswanath & Hsieh (1999)

The primary basis for the paper was the prediction of thermal conductivity for vegetable oils and its resulting affect on the Prandtl number. The group contribution model derived was based upon the semi-theoretical method derived by Viswanath and Klaas (1998),

$$\frac{\lambda}{\lambda_o} = \left(\frac{T}{T_o} \right)^{-2/3} \quad (11)$$

The problem with Equation (11) is that it was derived for operation between the normal melting point and boiling point. Thus, its range of applicability was quite small. However using it as a starting point to build upon, Rodenbush and co-workers combined the constants in the equation, coming up with a simplistic equation for the prediction of thermal conductivity via the group contribution method.

$$\lambda = DT^{-2/3} \quad (12)$$

In the above equation, D is the lumped constant $\lambda_o T_o^{2/3}$. It was proposed that this value be predicted for the different components via the group contribution method. The method uses 84 groups and 10 group corrections. Modelling was based on 228 liquids with 1487 experimental data points, which yielded an average absolute error of 2.5%.

Sastri and Rao (1999)

Sastri and Rao proposed a new equation similar to that of the Rackett equation for densities. Based upon their density equation and the trend followed by many previous thermal conductivity models, Sastri and Rao assumed a thermal conductivity form as follows:

$$\lambda = MN^{(1-T_r)^n} \quad (13)$$

In the above equation, M and N were defined as being dependent upon the compounds and n an index that should be constant for all liquids. Thus, using the form of the equation as used in the density prediction, the following model equation was derived:

$$\lambda = \lambda_B a^{[1 - ((1-T_r)/(1-T_{Br}))^n]} \quad (14)$$

In this equation, λ_B is calculated using the group contribution method:

$$\lambda_B = \sum \Delta\lambda_B + \sum \Delta\lambda_{corr} \quad (15)$$

In the above equation, $\Delta\lambda_B$ 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, which normally result in predicted thermal conductivities being much higher than those yielded by experimentation are. This method uses 32 groups and 7 group corrections.

This new method combined with the group contributions from the previously published method for predicting thermal conductivity at 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.

Discussion

Initial work done on the project included an extensive literature review to determine the extent of previous work done. This included reviewing available experimental data and correlative and predictive methods. Methods reviewed and chosen for consideration were benchmarked according to average deviations for predictions and applicability to different components. Group contribution methods were found to have the lowest deviations amongst all reviewed methods. To test this, two group contribution methods and two empirical correlations were chosen for implementation using the available thermal conductivity dataset. The group contribution methods chosen were those by Nagvekar and Daubert (1987) and Sastri and Rao (1993), and the empirical correlations chosen were those by Lakshmi *et al.* (1992) and Sato and Riedel (1977).

The experimental thermal conductivity data used were obtained from the DDB (Gmehling *et al.* 2009). This consisted of a data set of 100515 data points for 867 components. This data was filtered, retaining only data for the liquid phase. The data was then re-filtered, removing all components for which less than three data points were available, as for meaningful regression at least three data points were considered to be required. The resultant data set contains 50799 data points for 524 components. This data contains 38696 data points above 1.5atm (this is ~76% of the available data) and 12103 data points below 1.5atm.

A comparison of the dataset at pressures of above and below 1.5atm indicated that thermal conductivity is a weak function of pressure. However, there does seem to be a need for high-pressure data within industry. Moreover, this requirement is not satisfied with the temperature only dependent empirical correlations available.

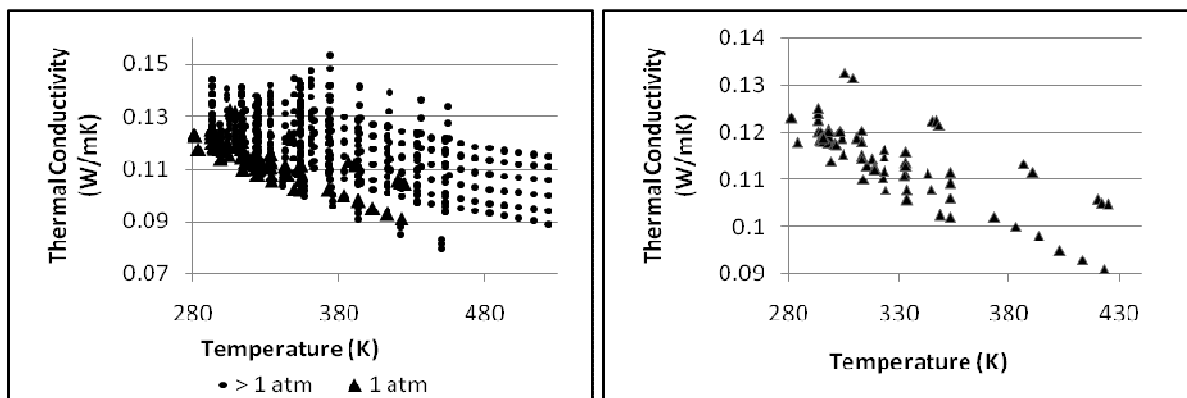


Figure 1: Thermal Conductivity Vs Temperature - ▲ data at 1 atm, ● data above 1 atm

The next step undertaken was the filtering of the data for any “bad” data. This may be data, which does not seem to follow any specific trend and any outliers or data that lies too far out from the trend of the specific dataset. From this filtering, it was noted that thermal conductivity does decrease linearly for most components, with certain components having a linear trend while others are slightly curved. This can be seen in Figure 1 Graph 2 above. Another problem noted was with outliers, which seemed to fit to their own trend curve. These were compared to higher pressure data and eliminated as required.

Pressure dependence was noted to have a positive gradient. However, it did not follow a linear trend. Thermal conductivity increases with pressure following an increasing parabolic trend, but as higher pressures are reached, this rate of increase decreases, just as does density as a function of pressure. Thus from this analysis of the data, it was proposed that a model for thermal conductivity should take the form:

$$\lambda(T, P) = \lambda(T_{Ref}) \times f(T - T_{Ref}) \times g(P - 101.3kPa) \quad (16)$$

As shown in Equation 15, the estimation method will consist of three parts, low-pressure thermal conductivity at a reference temperature, a low-pressure thermal conductivity dependence on temperature, and a dependence of thermal conductivity on pressure as a function of temperature.

Results of the methods of Nagvekar and Daubert (1987), and Sastri and Rao (1993) were compared to the available data set, obtaining absolute average deviations (AAD) of 16.64% and 14.11% respectively. This comparison was easily done using the methods implemented in the DDB Artist tool. The third method available in the DDB Artist (Lakshmi and Prasad 1992), which is an empirical correlation, yielded an AAD of 23.41%. The method by Sato and Riedel (1977) was implemented producing an AAD of 19.81%.

Table 1: Relative mean deviation (RMD) of thermal conductivity data for various homologous series' (NC – Number of components)

Group Name	Nagvekar & Daubert		Sastri & Rao		Lakshmi & Prasad		Sato & Riedel	
	NC	RMD %	NC	RMD %	NC	RMD %	NC	RMD %
Hydrocarbons	92	17.23	127	11.73	132	22.11	132	16.24
Aromatic Hydrocarbons	17	13.27	26	11.27	31	13.25	31	11.84
Halogen Compounds	39	17.91	80	26.27	80	47.45	80	16.42
Oxygen Compounds	118	15.96	206	13.56	212	32.02	212	26.91
Carboxylic Acids	8	7.81	9	15.47	9	18.88	9	15.71
Alcohols	40	13.88	49	13.36	51	26.48	51	22.20
Ethers	14	18.95	20	13.30	20	22.20	20	21.81
Esters	27	19.56	81	13.03	81	35.40	81	29.73
Ketones	16	14.14	19	13.14	19	25.93	19	22.86
Aldehydes	2	17.75	5	14.89	5	9.18	5	16.39
Nitrogen Compounds	29	21.01	25	12.68	45	31.85	45	32.38
Amines	15	38.83	20	14.14	20	13.95	20	21.76
Sulphur Compounds	0	-	2	10.63	2	5.58	2	3.33
Overall RMD	322	16.64	469	14.11	500	23.41	500	19.81

From the analysis of the four methods, it may be concluded that group contribution methods yield far better results than simple empirical correlations. The method by Nagvekar and Daubert (1987) is not applicable to all compounds. This deficiency may be accounted for by a lack of structural groups to account for some compounds. Similarly, the method by Sastri and Rao (1993) has more structural groups, which help account for a larger variety of compounds. The general correlation models allow all compounds to be accounted for, as there is no structural dependency.

Conclusions

Methods for the prediction of thermal conductivity have been investigated. Available thermal conductivity data was filtered and analysed, and possible form for a model (Equation (16)) has been suggested. The method shall follow the group contribution scheme and account for the temperature and pressure dependency of thermal conductivity.

Acknowledgements

The authors want to thank the South African National Research Foundation and DLR (BMBF) for financial support as well as DDBST GmbH for providing data and software support for this project.

References

- Assael, M.J., Trusler, J.P.M. and Tsolakis, T.F., *Thermophysical Properties of Fluids - An Introduction to their Prediction*, Imperial College Press, London (1998)
- Gmehling, J., Rarey, J. and Menke, J., <http://www.ddbst.com>, Dortmund Data Bank, Oldenburg (2009)
- Horvath, A.L., *Molecular Design - Chemical Structure Generation from the Properties of Pure Organic Compounds*, Elsevier, New York (1992)
- Klaas, D. M. and Viswanath, D.S., (1998), *Industrial & Engineering Chemistry Research*, 37, 2064-2068
- Lakshmi, D.S. and Prasad, D.H.L, (1992), *The Chemical Engineering Journal*, 48, 211-214
- Mathias, P.M., Parekh, V.S. and Miller, E.J., (2002), *Industrial & Engineering Chemistry Research*, 41 (5), 989-999
- Millet, J., Dymod, J.H. and Nieto de Castro, C.A., *Transport Properties of Fluids – Their Correlation, Prediction and Estimation*, Cambridge University Press, New York (2005)
- Moller, B.C., Rarey, J., and Ramjugernath, D., (2008), *Journal of Molecular Liquids*, 143, 52–63
- Nagvekar, M. and Daubert, T.E., (1987), *Industrial & Engineering Chemistry Research*, 26, 1362-1365
- Nannoolal, Y., Rarey, J. and Ramjugernath, D., (2007), *Fluid Phase Equilibria*, 252, 1-27
- Nannoolal, Y., Rarey, J. and Ramjugernath, D., (2008), *Fluid Phase Equilibria*, 269, 117-134
- Nannoolal, Y., Rarey, J. and Ramjugernath, D., (2009), *Fluid Phase Equilibria*, in Print
- Nannoolal, Y., Rarey, J., Ramjugernath, D. and Cordes, W., (2004), *Fluid Phase Equilibria*, 226, 45-63
- Nemzer, V.G., Nemzer, L.V. and Pugach, V.V., (1996), *Journal of Chemical and Engineering Data*, 41, 848-851
- Poling, B. E., Prauznitz, J.M. and O'Connell, J.P., *The Properties of Gases and Liquids*, McGraw-Hill, New York (2004)
- Rarey, J. and Cordes, W., (2002), *Fluid Phase Equilibria*, 201, 409-433
- Rodenbush, C.M., Viswanath, D.S. and Hsieh, F., (1999), *Industrial & Engineering Chemistry Research*, 38, 4513-4519
- Sastri, S.R.S. and Rao, K.K., (1999), *Chemical Engineering*, 74, 161-169
- Sastri, S.R.S. and Rao, K.K., (1993), *Chemical Engineering*, 100(8), 106-107.
- Smith, J.M., Van Ness, H.C. and Abbot, M.M., *Introduction to Chemical Engineering Thermodynamics*, McGraw-Hill, 7th Edition, New York (2005)