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A Critical Survey of Thermal Conductivity Literature Data for Organic Compounds at Atmospheric Pressure and an Equation for Aromatic Compounds

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Abstract

This work presents a wide literature survey of the available data of the experimental thermal conductivity data for organic liquids at the atmospheric pressure in the temperature range below normal boiling point and at saturation pressures for temperatures above the normal boiling point. The experimental data are collected for 136 pure compounds belonging to the following different families: refrigerant fluids, alkanes, alkenes, aromatics, cycloalkanes, cycloalkenes, ethers, esters, ketones, organic acids and alcohols. A reliable set of 4740 experimental data was finally selected. The range of temperatures and of thermal conductivity experimental values are analyzed and discussed. An equation for aromatic compounds is proposed. The equation is very simple and produces a noticeable improvement if compared with the existing equations.

Keyword: thermal conductivity; liquids; aromatics; new equation

1. Introduction

The thermal conductivity as defined by Fourier's equation, is a material's ability to transfer heat by means of conduction. For this reason, thermal conductivity is essential for the heat transfer knowledge and its estimation has been the subject of many studies. In order to provide a reliable database of the thermal conductivity for pure compounds, as a first step is useful a careful literature survey. For many compounds, thermal conductivity data can

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be found in reviews [1-2]. A complete and updated source of data can be found in the DIPPR 801 database [3]. For our data elaboration, we accepted data coming from all sources. In addition, a critical analysis of the published experimental data was performed.

One of the goal of the present work was to perform a statistical review of thermal conductivity data divided by families, paying particular attention to aromatics.

In the literature, there are equations based upon a material's specific property such as density and/or heat capacity [4,5]. These properties are all dependent upon temperature thus making impossible to use them for some fluids when not enough data are available; there are theoretical calculations considering the intermolecular distances [6] or the degree of association of liquids [1]; there are equations based upon the theory of group contribution which are very often not suitable for all compounds and rather laborious [7,8]; there are equations which make use of certain fixed parameters in order to describe thermal conductivity [7, 9-10]. Furthermore, the equations present in the open literature and based upon the corresponding states principle were considered [7, 9-10] so that the obtained results could be analyzed.

Another goal was to find a new physically grounded formula, based on Latini original formula [11], that minimizes the deviation between the predicted and the experimental data for aromatics. The Latini formula contains the factor Φ, called "golden ratio" related to the well know "sequence of Fibonacci" (F=1,1,2,3,5,8,13,21,34,...). It can be expressed as, $\Phi = \left(\sqrt{5}+1\right)\Big/_{2} = 1.618033\cdots$

Nomenclature

AAD%	Average absolute percent deviation	Φ	Golden ratio
M	Molecular mass	λ_{Exp}	Experimental thermal conductivity
n	Number of points	λ_{Calc}	Calculated thermal conductivity
T_b	Normal boiling temperature	ω	Acentric factor
T_{br}	Reduced normal boiling temperature	σ	Standard deviation
T_m	Normal melting temperature		
T_r	Reduced temperature		

2. Statistical analysis

In Fig. 1, all the collected data are reported as a function of the reduced temperature. From this figure, excluding few points for alcohols and carboxylic acids, a general common trend for all compounds as function of reduced temperature is evident. The whole database has been studied according to the an explanatory data analysis [12] with a statistical chart; this approach allows to suggest reliable models fitting the data, taking into account the structure and the outliers. In Figs 2-3, the statistical summary for thermal conductivity and reduced temperature for the entire

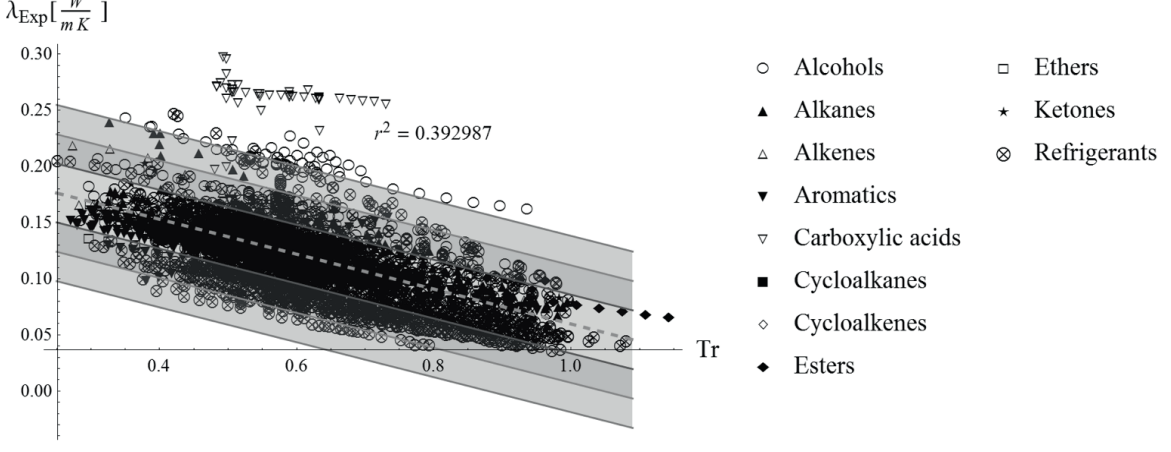


Figure 1: Scatter Plot of experimental thermal conductivity data versus reduced temperature. Confidence bands at ±σ, ± 2 σ and ± 3 σ are also reported

dataset are reported.

On the left, the histogram that underlines the smooth distribution of the values of thermal conductivity and reduced temperature is reported; it allows to see where the majority of values falls in a measurement scale, and how

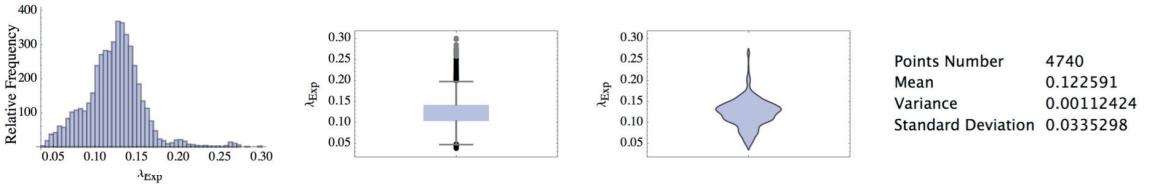


Figure 2:Statistical summary for thermal conductivity

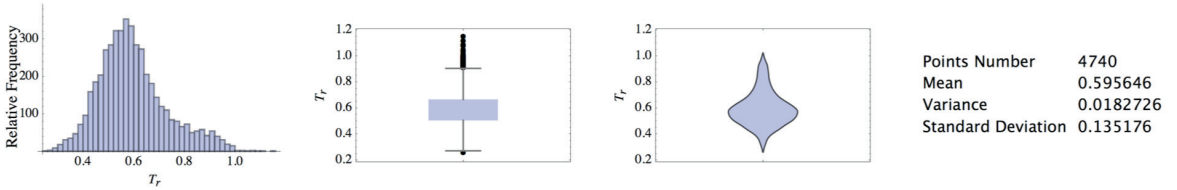
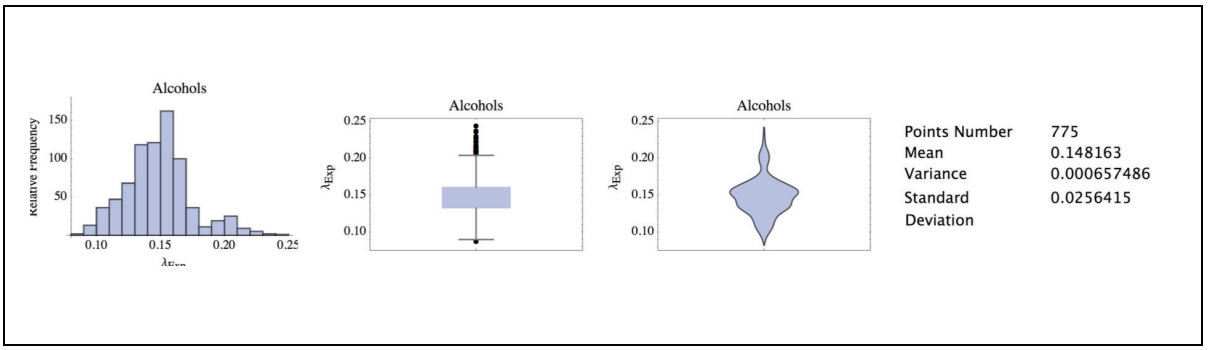
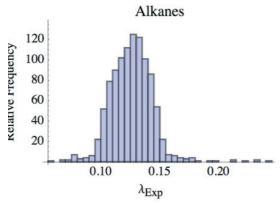


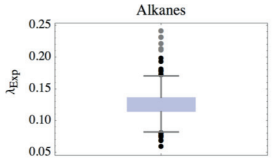
Figure 3:Statistical summary for reduced temperature

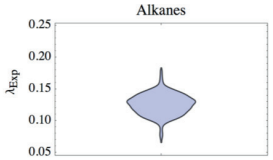
much variation present is. The middle chart is the box whisker chart, that helps in understanding if the data points are clustered around some central value, where are the lower and upper quartile ad the median; this chart contains also the representation of some outliers signed out of the whiskers. The right chart shows the distribution chart that draws a representation of the distribution of values in each point. Then, the summary of the number of points, the mean, the variance and the standard deviation are also reported.

After the general analysis, a more detailed family by family analysis was performed, as shown in Fig. 4.

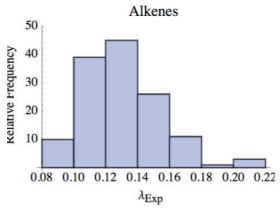


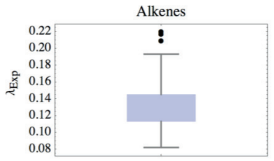


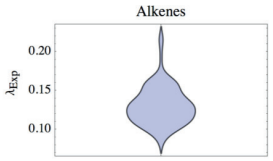




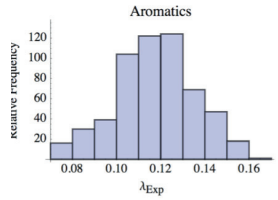
Points Number	1025
Mean	0.1259
Variance	0.000332916
Standard Deviation	0.018246

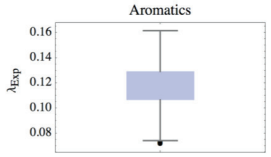


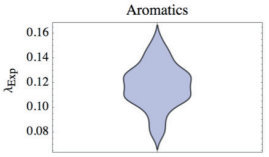




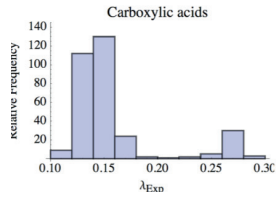
Points Number	135
Mean	0.130141
Variance	0.000593009
Standard Deviation	0.0243518

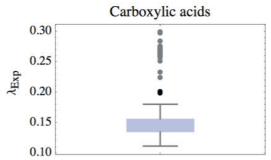


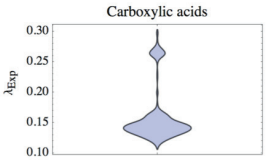




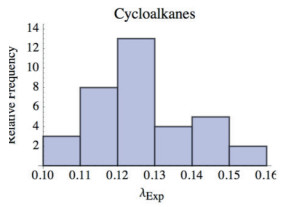
Points Number	570
Mean	0.117383
Variance	0.000324128
Standard Deviation	0.0180035

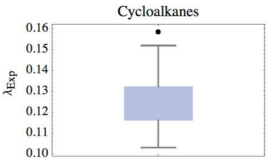


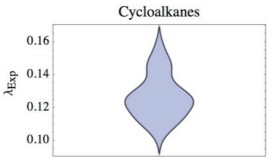




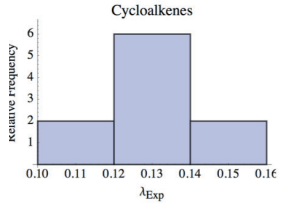
Points Number	318
Mean	0.157553
Variance	0.00182336
Standard Deviation	0.0427008

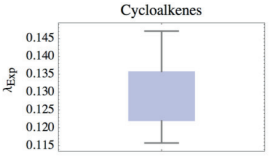


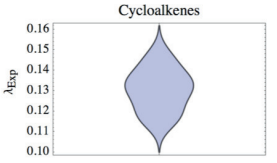




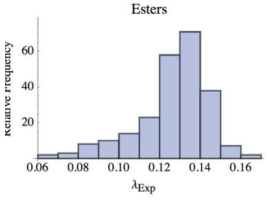
Points Number	35
Mean	0.126207
Variance	0.000179009
Standard Deviation	0.0133794

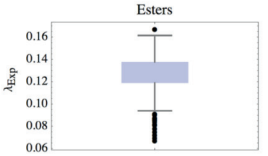


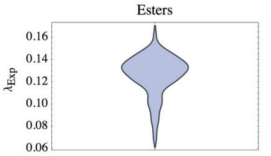




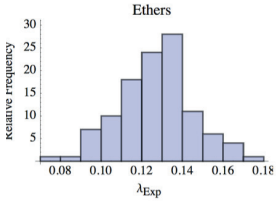
Points Number	10
Mean	0.130313
Variance	0.000108396
Standard Deviation	0.0104113

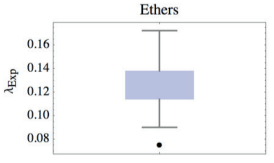


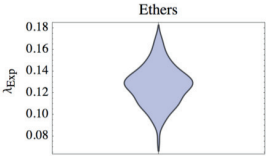




Points Number	236
Mean	0.126133
Variance	0.000320984
Standard Deviation	0.017916







Points Number	111
Mean	0.126808
Variance	0.000326893
Standard Deviation	0.0180802

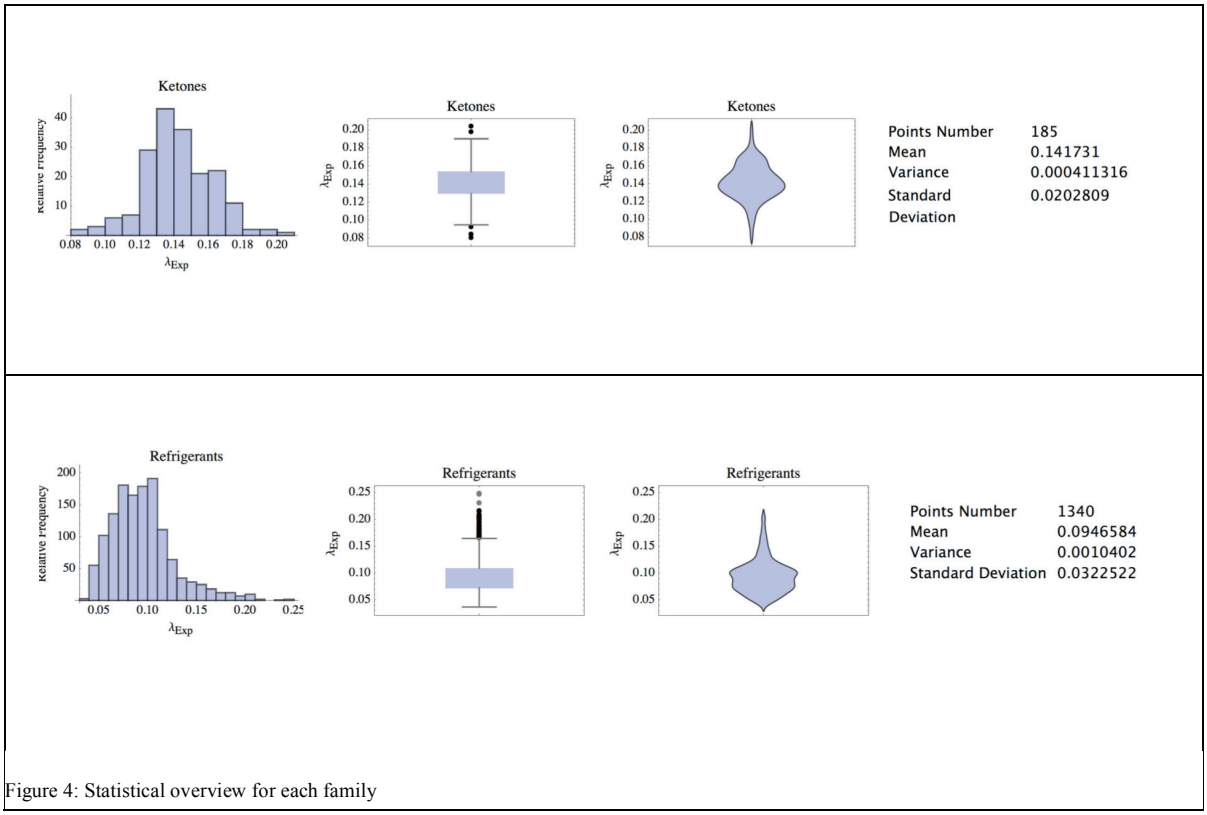


Figure 4: Statistical overview for each family

From Fig.4, it is possible to point out that the main part of the experimental data is distributed from 0.03 to 0.18 W/mK and that the maximum number of experimental data was obtained at around λ= 0.12-0.13 W/mK, with the exception of refrigerants, ketones, aromatics, alcohols and carboxylic acids.. It is also evident that the families that show the higher number of experimental data are refrigerants, alkanes, alcohols and aromatics. Furthermore, all the distributions are quite regular excluding points at high value of thermal conductivity for carboxylic acids.

3. The equation for aromatics

After the general statistical analysis, the research was specifically oriented to aromatic family containing a benzene ring of six carbon atoms, exception doing for naphtalene and phenanthrene that contain a double ring.
To find potential outliers, the scatter plot for each compound was reported in Fig. 5. The experimental data of 1,3,5 –Tris (1-Methylethyl) clearly showed anomalous behaviour if compared with the rest of the experimental data.

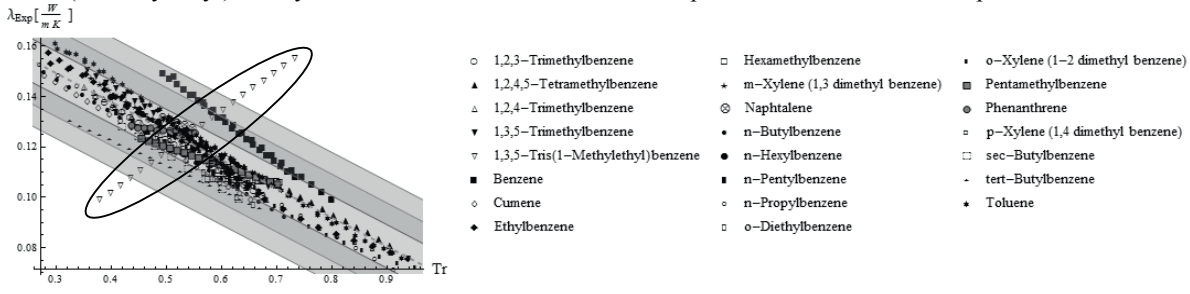


Figure 5. Scatter Plot of experimental thermal conductivities as a function of reduced temperature

In table 1, an overview of the experimental data ranges is reported.

Table 1. Summary of the experimental data ranges for the aromatic compounds and coefficients for Eq (1)

Name	N° points	T range	λ range [W/mK]	a	A	AAD%
1-2-3-Trimethylbenzene	20	247.79- 449.27	0.1003- 0.1399	0.5	0.107	0.58
1-2-4-5-Tetramethylbenzene	40	352.38- 613.15	0.0809- 0.1264	0.4	0.114	0.85
1-2-4-Trimethylbenzene	20	229.33- 442.53	0.099- 0.1439	0.5	0.108	0.42
1-3-5-Trimethylbenzene	20	228.42- 437.89	0.1042- 0.1505	0.5	0.113	0.56
1-3-5-Tris(1-Methylethyl)benzene	20	265.75- 511.15	0.099- 0.1553	-0.5	0.135	1.25
Benzene	37	278.68- 450	0.099- 0.1492	0.5	0.129	0.86
Cumene	20	177.14- 413.15	0.0992- 0.1485	0.5	0.104	0.43
Ethylbenzene	41	178.2- 580	0.0755- 0.1574	0.5	0.110	1.23
Hexamethylbenzene	20	438.65- 536.6	0.106174- 0.107448	0.1	0.107	0.63
m-Xylene (1-3 dimethyl benzene)	35	225.3- 580	0.0762- 0.1474	0.5	0.110	1.34
Naphtalene	5	370- 410	0.128- 0.132	0.5	0.116	0.93
n-Butylbenzene	20	185.3- 473.15	0.0923- 0.1499	0.5	0.105	0.45
n-Hexylbenzene	9	280- 440	0.113- 0.14	0.4	0.115	0.34
n-Pentylbenzene	9	280- 430	0.104- 0.134	0.5	0.106	0.13
n-Propylbenzene	20	173.55- 583.15	0.0713- 0.1526	0.5	0.108	1.11
o-Diethylbenzene	9	280- 440	0.097- 0.132	0.4	0.106	2.68
o-Xylene (1-2 dimethyl benzene)	36	247.98- 600	0.0721- 0.1429	0.5	0.111	1.33
Pentamethylbenzene	20	327.45- 504.55	0.1056- 0.1238	0.3	0.111	0.56
Phenanthrene	11	380- 480	0.126- 0.129	0.1	0.124	0.36
p-Xylene (1-4 dimethyl benzene)	35	286.41- 580	0.076- 0.1325	0.5	0.111	1.28
sec-Butylbenzene	8	280- 420	0.099- 0.128	0.5	0.102	0.59
tert-Butylbenzene	20	215.27- 442.3	0.0957- 0.1303	0.4	0.101	0.19
Toluene	95	178.18- 550	0.076- 0.1614	0.5	0.115	1.29

As a starting point, the recent Latini Equation [11] was considered

$$\lambda = A \cdot \left(\sqrt{5} \frac{\left(\Phi - T_r\right)^2}{\left(\Phi + T_r\right)} \right)^a \tag{1}$$

where A and a are tuned for each compound. The obtained coefficients are listed in the Table 1, where the AAD % according to eq.2 are also reported

$$AAD\% = \frac{1}{n} \sum_{i=1}^{n} \left[\left| \frac{\left(\lambda_{\exp}^{i} - \lambda_{calc}^{i}\right)}{\lambda_{\exp}^{i}} \right| \right] \cdot 100 \tag{2}$$

Since the two parameters a and A are tuned for each compound, Eq. (1) shows very low deviations. The aim of this paper was to find a version of Eq. (1) without losing in terms of prediction capability.
At the beginning, a non linear regression of the coefficient a, varying A, was performed, as reported in Table 2. In this way, having just one varying parameter, slightly higher deviations were observed. The coefficients are reported in Table 2, attempt 1.

Table 2. Summary of the coefficients

	a	A
Attempt 1	0.434	as reported in Table 1
Attempt 2	0.410	0.156
Attempt 3	0.469	as reported in Table1
Attempt 4	0.434	0.158

As second step, both a and A were regressed for the complete set of data. The exponents a and the factors A are reported in Table 2, attempt 2.
Deviations for the equation (1), attempts 1 and 2 are summarized in Table 3.

Table 3. AAD% comparison between Eq. (1), Eq. (1) Attempt 1 and Eq. (1) Attempt 2

Fluid	AAD% Eq.(1)	AAD% Eq. (1) Attempt 1	AAD% Eq. (1) Attempt 2
1,2,3-Trimethylbenzene	0.58	1.71	2.91
1,2,4,5-Tetramethylbenzene	0.85	0.86	1.51
1,2,4-Trimethylbenzene	0.42	1.54	2.56
1,3,5-Trimethylbenzene	0.56	1.91	2.77
1,3,5-Tris(1-Methylethyl)benzene	1.25	26.46	20.35
Benzene	0.86	1.99	11.80
Cumene	0.43	1.96	5.39
Ethylbenzene	1.23	2.51	3.13
Hexamethylbenzene	0.63	3.76	3.82
m-Xylene (1,3 dimethyl benzene)	1.34	2.32	2.81
Naphtalene	0.93	1.43	4.86
n-Butylbenzene	0.45	1.98	4.94
n-Hexylbenzene	0.34	1.17	1.53
n-Pentylbenzene	0.13	1.51	4.17
n-Propylbenzene	1.11	1.83	4.36
o-Diethylbenzene	2.68	2.10	6.56
o-Xylene (1-2 dimethyl benzene)	1.33	2.65	3.60
Pentamethylbenzene	0.56	2.63	2.68
Phenanthrene	0.36	10.55	2.34
p-Xylene (1,4 dimethyl benzene)	1.28	1.92	2.82
sec-Butylbenzene	0.59	1.62	8.66
tert-Butylbenzene	0.19	1.19	12.00
Toluene	1.29	1.97	3.00
Mean	0.95	3.02	4.74

From Table 3, it is evident, as expected, that the higher value of AAD% is for 1,3,5 –Tris (1-Methylethyl). Then, regressions were repeated after removing this set of data. Attempts 1 and 2 became respectively attempts 3 and 4. The respective coefficients are also reported in Table 2.
To test the validity of the new equation, for comparison three different literature equations were considered.

The Sato-Riedel equation [7] it is a rather simple equation that needs the knowledge of the experimental temperature, the normal boiling point temperature, the molecular mass, the critical temperature as follows:

$$\lambda = \frac{1.1053}{M^{1/2}} \frac{3 + 20(1 - T_r)^{2/3}}{3 + 20(1 - T_{br})^{2/3}} \tag{3}$$

The Sheffy and Johnson equation [9] is also a very simple equation, containing only the experimental temperature, the melting temperature and the molecular mass as physical parameters:

$$\lambda = 1.951 \frac{1 - 0.00126(T - T_m)}{T_m^{0.216} M^{0.3}} \tag{4}$$

However, the Sato-Riedel equation and the Sheffy and Johnson equation, probably because of their simplicity, showed rather high deviations for almost all the analyzed compounds, as shown in Table 4

It is important to state that none of the presented methods is able to predict in a reliable way the thermal conductivity behaviour near the critical point. In order to overcome this point and to cover a significantly wider number of chemical families, a recent equation was proposed by Gharagheizi et al. [10] adopting a GEP [13] mathematical strategy:

$$\lambda = 1 \cdot 10^{-4} \left[10 \cdot \omega + 2P_c - 2T + 4 + 1.908\left(T_b + \frac{1.009 \cdot B^2}{M^2}\right) + \frac{3.9287 \cdot M^4}{B^4} + \frac{A}{B^8} \right] \tag{5}$$

where

$$A = 3.8588 M^8 (1.0045B + 6.5152M - 8.9756) \tag{6}$$

and

$$B = 16.0407M + 2T_b - 27.9074 \tag{7}$$

To test the goodness of the existing equations, deviations between the experimental thermal conductivities and the predicted ones were calculated and reported in Table 4.

Table 4. AAD% comparison between different equations.

Fluid Name	N. Points	AAD% Eq.(1)	AAD% Eq. (1) Attempt 3	AAD% Eq.(1) Attempt 4	AAD% Eq. (3)	AAD% Eq.(4)	AAD% Eq. (5)
1,2,3-Trimethylbenzene	20	0.58	0.95	2.88	2.11	2.59	6.66
1,2,4,5-Tetramethylbenzene	40	0.85	1.82	2.61	13.16	2.12	3.71
1,2,4-Trimethylbenzene	20	0.42	0.62	2.56	2.69	2.45	5.41
1,3,5-Trimethylbenzene	20	0.56	1.09	2.73	1.85	2.28	0.95
Benzene	37	0.86	1.37	12.37	2.16	12.54	3.24
Cumene	20	0.43	0.74	5.66	7.56	4.41	8.10
Ethylbenzene	41	1.23	1.64	2.33	5.36	4.64	3.93
Hexamethylbenzene	20	0.63	4.08	3.74	10.24	3.15	4.66
m-Xylene (1,3 dimethyl benzene)	35	1.34	1.71	2.12	5.72	7.63	4.76
Naphtalene	5	0.93	0.92	4.85	10.69	6.02	1.03
n-Butylbenzene	20	0.45	0.83	5.03	0.86	1.71	4.51
n-Hexylbenzene	9	0.34	2.02	1.50	9.93	14.26	3.33
n-Pentylbenzene	9	0.13	0.76	4.13	2.46	6.24	2.71
n-Propylbenzene	20	1.11	0.75	3.85	4.56	1.15	3.60
o-Diethylbenzene	9	2.68	1.74	6.45	1.29	2.62	5.16

o-Xylene (1-2 dimethyl benzene)	36	1.33	1.77	2.83	5.60	9.23	6.56
Pentamethylbenzene	20	0.56	3.23	2.87	6.03	3.69	4.53
Phenanthrene	11	0.36	11.68	2.50	14.42	16.37	7.32
p-Xylene (1,4 dimethyl benzene)	35	1.28	1.41	2.15	6.15	13.82	9.40
sec-Butylbenzene	8	0.59	1.00	8.62	1.60	2.08	5.01
tert-Butylbenzene	20	0.19	2.27	12.13	4.61	6.57	7.83
Toluene	95	1.29	1.31	2.80	5.58	8.48	4.80
Total	550	18.15	43.71	96.72	124.63	134.03	107.21
Mean	-	0.95	1.75	4.06	5.69	6.59	5.03

From Table 4 it is evident that the simplification of Eq. (1) by Eq. (1) attempt 3 and 4 was successfully obtained with a minimal lost in terms of deviations. Other equations existing in the literature generally showed higher deviations for aromatics. However, in as to be considered that literature equations were not specifically oriented to aromatics, but to a generic organic compound. Furthermore, the Eq. (1) attempt 3 and 4 are very simply, containing only reduced temperature as physical property.

4. Conclusions

After a careful literature survey, the available data of the experimental thermal conductivity data were collected and statistically analyzed. Particular attention was then focused on aromatic compounds. Experimental data for aromatics were regressed with the most reliable semi-empirical correlating methods based on the corresponding states theory existing in the literature. A new and simple equation was developed for the thermal conductivity calculation of aromatics.

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