Thermophysical properties of fluids: dynamic viscosity and thermal conductivity

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Abstract. Thermophysical properties of fluids strongly depend upon atomic and molecular structure, complex systems governed by physics laws providing the time evolution. Theoretically the knowledge of the initial position and velocity of each atom, of the interaction forces and of the boundary conditions, leads to the solution; actually this approach contains too many variables and it is generally impossible to obtain an acceptable solution. In many cases it is only possible to calculate or to measure some macroscopic properties of fluids (pressure, temperature, molar volume, heat capacities…). The ideal gas "law," PV = nRT, was one of the first important correlations of properties and the deviations from this law for real gases were usefully proposed. Moreover the statistical mechanics leads for example to the "hard-sphere" model providing the link between the transport properties and the molecular size and speed of the molecules. Further approximations take into account the intermolecular interactions (the potential functions) which can be used to describe attractions and repulsions. In any case thermodynamics reduces experimental or theoretical efforts by relating one physical property to another: the Clausius-Clapeyron equation provides a classical example of this method and the PVT function must be known accurately. However, in spite of the useful developments in molecular theory and computers technology, often it is usual to search for physical properties when the existing theories are not reliable and experimental data are not available: the required value of the physical or thermophysical property must be estimated or predicted (very often estimation and prediction are improperly used as synonymous). In some cases empirical correlations are useful, if it is clearly defined the range of conditions on which they are based. This work is concerned with dynamic viscosity \( \mu \) and thermal conductivity \( \lambda \) and is based on clear and important rules to be respected when a prediction or estimation method is proposed.

1. Introduction
An acceptable estimation method of a given thermophysical property must be characterized as follows:
- the values of the thermophysical property must be reliable for pure substances and for mixtures at any given temperature, pressure and composition;
- the phase (solid, liquid, or gas) must be clearly indicated;
- the number of input data has to be minimized;
- the ranges of the probable errors must be clearly indicated;
- the computation time must be minimized.

Obviously very few of the methods satisfy these conditions, and among the different molecular theories useful for data correlation, a theory is particularly helpful: the law of corresponding states or the corresponding-states principle, originally presented by macroscopic arguments, but successively grounded on a molecular basis. The law of corresponding states (van der Waals [1]) is based on the hypothesis that equilibrium properties are linked in a universal way with the critical properties, and allows the development of correlations and estimation methods: two-parameter corresponding states.
theory asserts that if pressure, volume, and temperature are divided by the corresponding critical properties, the function relating reduced pressure to reduced volume and reduced temperature is the same for all substances. Of course small molecules with spherical symmetry are satisfactorily covered by a two-constant law of corresponding states, but complex, non-spherical and weakly polar molecules do not follow the law as well, and a third parameter, for example the acentric factor $\omega$, has to be added. Summarizing, good correlations exist for nonpolar fluids, but analogous correlations are often not available for polar fluids or show very low reliability.

Another useful method has to be presented: a macroscopic property clearly depends upon the molecular structure and can be estimated by the group contributions method (generally by an algebraic operation that sums the contributions from the molecule’s parts).

In any case reliable experimental data are preferred with respect to results obtained by estimation methods and several data banks are available containing experimental and calculated data. Some estimation methods are based on theory with empirical corrections, others are based on empirical generalizations and totally empirical correlations are also useful when theory or general principles are not acceptable.

Several estimation methods require parameters that are characteristic of the single pure compound or of the constituents of a mixture and classical examples are critical temperature $T_c$, normal freezing point $T_f$, and the normal boiling point $T_b$. Pure component properties include for example the vapor-liquid critical properties, atmospheric boiling and freezing temperatures, dipole moments, liquid molar volume, heat capacities, acentric factor and so on. These properties are calculated by several methods and often can be compared with the corresponding experimental values. The properties of a molecule are usually calculated by the contributions of its elements (atom contributions, bond contributions, group interaction contributions…). Some examples are presented in this work.

1.1. Critical Properties: Method of Joback [2,3]

The relations for the critical properties are as follows:

\[
T_c(K) = T_b [0.584 + 0.965(\sum_k N_k(tck)) - (\sum_k N_k(tck))^2]^{-1}
\]

\[
P_c(\text{bar}) = [0.113 + 0.0032 N_{\text{atoms}} - \sum_k N_k(pck)]^{-2}
\]

\[
V_c(\text{cm}^3\text{mol}^{-1}) = 17.5 + \sum_k N_k(vck)
\]

where tck, pck and vck are referred to the contributions. The group identities and Joback’s values for contributions to the critical properties are tabulated in [4]. $T_c$ needs the value of the normal boiling point $T_b$. The Joback method for critical properties is reliable for $T_c$ (errors usually less than 5%), but there is a significant increase in error when estimated (and not experimental) values of $T_b$ are used. For the calculated values of $P_c$ the reliability is less. For $V_c$, the average error is generally greater than 5%.

1.2. Critical Properties: Method of Constantinou and Gani [5]

The method of Constantinou and Gani for critical properties is based on an advanced group contribution method (“second order” level):

\[
T_c(K) = 181.128 \ln[\sum_k N_k(tc1k) + W \sum_j M_j(tc2j)]
\]

\[
P_c(\text{bar}) = [\sum_k N_k(pc1k) + W \sum_j M_j(pc2j) + 0.10022]^{-2} + 1.3705
\]

\[
V_c(\text{cm}^3\text{mol}^{-1}) = -0.00435 + [\sum_k N_k(vc1k) + W \sum_j M_j(vc2j)]
\]
In this case $T_c$ does not depend on the value of $T_b$. $N_k$ is the number of first-order groups of type $k$ in the molecule; the labels 1 and 2 are referred to the first-order and second-order group; $M_j$ is the number of second-order groups of type $j$ in the molecule; the value of $W$ is 0.0 and 1.0 respectively for first-order and second-order calculations.

The first-order contributions are usually sufficient. The second-order contributions are useful, but in some cases they are very small and can worsen the results. Several other estimation methods for critical properties exist in the literature and can be divided into two classes: the first class is based on so-called factor analysis (correlations built from data of measurable, macroscopic properties such as densities, molecular weight, boiling temperature, etc), the second class is based on so-called molecular descriptors which are not normally measurable.

1.3. Normal boiling point $T_b$ and normal freezing point $T_f$

Some estimation methods need $T_b$ as input information for the calculation of $T_c$ and obviously the errors can increase (greater than 10%).

1.3.1.-Method of Joback [3, 4]

Joback, using a group contribution scheme with several new functional groups, proposes for $T_f$ and $T_b$ the following relations:

\[
T_f = 122 + \sum k N_k(tfk)
\]

\[
T_b = 198 + \sum k N_k(tbk)
\]

The labels $tfk$ and $tbk$ are for the contributions to $T_f$ and $T_b$, respectively. The errors are usually greater than 10%.

2. Viscosity of gases and liquids

Dynamic viscosity $\mu$ is a measure of the internal fluid friction; molecular theories for the gases were satisfactorily developed by non equilibrium statistical mechanics and kinetic theory, but the corresponding theories for the liquids are far away from the desired accuracy in the results. In this paper the discussion is concerned with newtonian fluids, that is with fluids in which the viscosity does not depend upon either the magnitude of the shearing stress or velocity gradient.

Estimation methods are presented able to:
- correlate viscosities with temperature and pressure;
- estimate viscosities when no experimental data are available;
- estimate the viscosities of mixtures.

2.1. Low-pressure gas viscosity, simple theoretical approach and estimation methods

The different gas viscosity estimation methods are based on the Chapman-Enskog theory [6] or on the law of corresponding states. In a very simple way a gas can be modeled to obtain general relations among viscosity, temperature, pressure, and molecular size. The Chapman-Enskog model shows:

\[
\mu = \frac{(26.29)(MT)^{1/2}}{\sigma^2\Omega_v}
\]

where $\mu$ is in $\mu P$, $M$ is the molecular weight in g/mol, $T$ the temperature in $K$, $\sigma$ the so-called hard-sphere diameter in Å and $\Omega_v$ a particular collision integral, different for each given intermolecular potential model.

2.1.1-Method of Chung et al [7,8]
Chung et al start from eq (9) and obtain:

$$\mu = 40.785 \cdot \frac{F_c(MT)^{1/2}}{V_c^{1/3} \Omega_v}$$  \hspace{1cm} (10)$$

where $\mu$ is in $\mu$P, $M$ is the molecular weight in g/mol, $T$ is the temperature in K, $V_c$ is the critical volume in cm$^3$/mol, $\Omega_v$ the collision integral and $F_c$ a factor necessary to take into account the molecular shapes and polarities of dilute gases. The average absolute error appears to be about 1.9%.

### 2.1.2. Corresponding states methods

Starting from eq(9) Lucas [9] obtains:

$$\mu^* = \left[0.807T_r^{0.618} - 0.357 \exp(-0.449T_c) + 0.340 \exp(-0.458T_c) + 0.018\right] F_p^0 P_Q^0$$  \hspace{1cm} (11)$$

where $\mu$ is in $\mu$P, $T_r$ is the reduced temperature $T/T_c$, $\xi=0.176\left(\frac{T_c}{M^4 P_c}\right)^{1/6}$, $M$ is the molecular weight in kg/kmol, $P_c$ is the critical pressure in N/m$^2$. $F_p^0$ and $P_Q^0$ are correction factors introduced to take into account polarity and quantum effects.

Reichenberg [10,11] has suggested an other corresponding states relation for low-pressure gas viscosity of organic compounds which appears as follows:

$$\mu = \frac{M^{1/2} T}{a^4 \left[1+(4/T_c)\right]^{1/2} \left[1+0.36T_r(T_r-1)^{1/6} \frac{T_r+270\mu^2}{T_c+270\mu^2}\right]}$$  \hspace{1cm} (12)$$

$\mu$ is in $\mu$P, $T$ is the temperature in K, $T_r$ is the reduced temperature $T/T_c$, $M$ is the molecular weight in kg/kmol, $\mu^*$ is a particular reduced dipole moment and $a^*$ depends upon the groups of the different compounds. The errors are usually in the range 0.5% to 1.5% for nonpolar compounds and 2% to 4% for polar compounds.

### 2.2. The pressure dependence of the viscosity of pure gases

Usually, at reduced temperatures $T_r > 1.5$ and reduced pressures $P_r < 2$, the viscosity shows a small dependence on the pressure; on the contrary if $1 < T_r < 1.5$ and $P > P_c$, pressure has a very large effect on viscosity. Near the critical point $T_c$, the viscosity diverges and its value is larger than expected, even if this effect (the so-called critical enhancement) is smaller than the analogous enhancement for thermal conductivity. The thermal conductivity usually increases by a factor of two near the critical point, while the increase in viscosity is about 1%.

At high reduced pressures the viscosity behavior appears to simulate a liquid state, and an increase in temperature results in a decrease in viscosity. Finally, at very high-reduced temperatures, again pressure has little effect and viscosities increase with temperature. This behavior strongly suggests that density is a variable to take into account for a correct description of viscosity at high pressures.

Very few theoretical studies were developed to estimate the dependence of the viscosity on the pressure; Chapman and Cowling [6], following the theory due to Enskog, faced the problem for dense gases assuming that the gas consists of dense hard spheres and behaves as a low-density hard-sphere system when the events occur at a faster rate owing to the higher rates of collision.

### 2.3. Viscosities of gas mixtures at low pressures

The kinetic theory developed by Chapman and Enskog [6] can be extensively used to calculate the viscosity of low-pressure multicomponent mixtures. The formulas are very complicated and are rarely used without strong simplifications. Some methods are presented in [4] and usually they are interpolative (the viscosities of the pure compounds must be available).
Lucas [9] and Chung et al. [7,8] proposed estimation methods over the entire range of composition. The errors by these two methods are higher than those of the interpolative techniques, but usually less than ±5%. Such errors could be reduced if pure component viscosity data are available and employed by a simple linear correction scheme.

2.4. Viscosities of gas mixtures at high pressures
The methods due to Lucas [9] and Chung et al [7,8] show smaller accuracies when applied to gas mixtures at high pressures. The accuracies are very poor in the critical region or at densities close to those of a liquid at the same temperature. The lack of accurate high-pressure gas mixtures experimental viscosity data does not allow accurate tests, but reasonable absolute average deviations of 8% to 9% for both polar and nonpolar dense gas mixtures can be supposed. In any case it is possible, when using the above cited methods, to program the same relations for low-pressure pure gases, low-pressure gas mixtures, and high-pressure pure gases. One program can cover all those cases and high-pressure gas mixtures.

2.5. Liquid viscosity
In many cases it is necessary to determine the liquid dynamic viscosity from experimental data when such data exist. The viscosities of liquids are much larger than those of gases at the same temperature. For example, the viscosity of liquid benzene near the normal boiling point (353.4 K) is more than 30 times the vapor viscosity, and at lower temperatures, this ratio increases. Moreover, below $T_c$, low-pressure gas viscosities vary in a nearly linear way with the temperature; on the contrary low-pressure liquid viscosities show a strong curvature which can be eliminated if the logarithm of the viscosity is plotted as a function of the reciprocal absolute temperature. Usually the normal boiling point for organic compounds would be at a value of $T_r^{-1} \approx 1.5$. For temperatures below the normal boiling point ($T_r^{-1} > 1.5$), the logarithm of the viscosity varies linearly with $T_r^{-1}$, but above the normal boiling point, this is not verified. In the nonlinear region, several corresponding states estimation methods have been suggested. In the linear region most of the corresponding states methods are not reliable, and generally the estimation methods are used to emphasize the effects of the chemical structure. At comparable reduced temperatures, viscosities of polar fluids are higher than those of nonpolar liquids. For engineering purposes it is preferable to use the ratio of the dynamic viscosity to the density, that is the kinematic viscosity, normally expressed in $\text{m}^2/\text{s}$ or in stokes. The kinematic viscosity $\nu$ decreases with increasing temperature so that that $\ln \nu$ is nearly linear in temperature for both the saturated liquid and vapor.

Summarizing, pure liquid viscosities at high reduced temperatures are normally correlated with some extension of the law of corresponding states. At lower temperatures, several methods are empirical in nature and based on a group contribution approach. Liquid mixture correlations are essentially mixing rules relating pure component viscosities to composition.

2.5.1. Liquid viscosity at high pressure
Lucas [12] has suggested the following equation:

$$\frac{\mu}{\mu_{sL}} = \frac{1+D\left(\frac{\Delta P_r}{2118}\right)^A}{1+C\ln \Delta P_r}$$

(13)

$\mu = \text{viscosity of the liquid at pressure } P$

$\mu_{sL} = \text{viscosity of the saturated liquid at } P_{vp}$

$\Delta P_r = (P - P_{vp})/P_c$
\( \omega = \text{acentric factor} \)

\[ A = 0.9991 - [4.674 \times 10^{-4}/(1.0523 T^{0.03877} - 1.0513)] \]

\[ D = [0.3257/(1.0039 - T^{2.573})^{0.2906}] - 0.2086 \]

\[ C = -0.07921 + 2.1616 T - 13.4040 T^2 - 84.8291 T^3 + 96.1209 T^4 - 59.8127 T^5 + 15.6719 T^6 \]

Lucas tested 55 polar and non polar liquids and claimed errors less than 10%.

2.5.2. Liquid viscosity as function of temperature

The viscosities of liquids decrease with the increasing temperature in isobaric conditions and along the saturation line. From the freezing point to close the normal boiling point, it is a good approximation to assume a linear relation between \( \ln \mu \) and the reciprocal of the absolute temperature; i.e.:

\[ \ln \mu = A + \frac{B}{T} \]  

(14)

This simple equation is usually referred to as the Andrade equation \([13,14]\). Several modifications of Eq. (14) have been proposed to improve its accuracy by including some function of the liquid molar volume or introducing the use of a third constant. In conclusion, from the freezing point to close the normal boiling point, Eq. (14) is a reliable function correlating the liquid viscosity with the temperature even if two datum points are required. At low temperature, in order to estimate the liquid viscosity, structural-sensitive parameters are often employed which are valid only for certain homologous series or are found from group contributions. These methods often use some extension of Eq. (14) and are acceptable for reduced temperatures less than about 0.75. In literature are also described techniques employing corresponding states methods. These methods are not particularly reliable.

2.5.3. Liquid viscosity estimation at high temperatures

Low-temperature viscosity correlations usually assume that \( \ln \mu \) is a linear function of reciprocal absolute temperature. Because above \( T_r \) near to 0.7 this relation is not accurate, from about \( T_r \approx 0.7 \) to near the critical point, some estimation methods based upon corresponding states principle are proposed which are similar to those used for gases. In particular Sastri \([4]\) proposed:

\[ \ln \mu = \left[ \ln \left( \frac{\ln \mu_b}{\ln (\alpha \mu_b)} \right) \right]^0 \ln (\alpha \mu_b) \]  

(15)

where \( \mu \) is in nPa-s, \( \mu_b \) is the viscosity at \( T_b \), the value of \( \alpha \) is 0.1175 for alcohols and 0.248 for other compounds and \( \phi = (1 - T_b)/(1 - T_c) \).

Sastri claimed average deviations of 10% for \( T_r > 0.9 \) and 6% for \( T_r < T_c \). The problem of joining high-temperature and low-temperature estimation methods for liquid viscosities should be faced.

2.5.4. Viscosity of liquid mixtures

All the correlations for liquid mixture viscosity are generally accurate at reduced temperatures (of the pure components) less than 0.7, when pure liquid and liquid mixture viscosities strongly depend upon the structure of the constituent molecules. The trend of the curve of viscosity as a function of composition can be nearly linear for so-called ideal mixtures, but mixtures containing alcohols and/or
water sometimes show a maximum and/or a minimum. Substantially the methods to estimate liquid mixture viscosities need the knowledge of the values of the viscosities of the pure components and so the methods are interpolative. A simple example of a correlation for the low-temperature liquid mixture viscosity is given by the correlation of Grunberg and Nissan [15]:

\[
\ln \mu_m = \sum_i x_i \ln \mu_i + \frac{1}{2} \sum_{i=1}^n \sum_{j=1}^n x_i x_j G_{ij}
\]  

where \( x \) represents the liquid mole fractions and \( G_{ij} \) is an interaction parameter depending on the components and on the temperature.

3. Thermal conductivity of gases and liquids

Some estimation techniques for thermal conductivities \( \lambda \) of gases and liquids are covered in this section with the effects of temperature and pressure. Estimation techniques for gas and liquid mixtures are also discussed. The units used for thermal conductivity are W/(m K).

3.1. Theory of thermal conductivity of monoatomic and polyatomic gases

A detailed treatment for monatomic gases, without rotational or vibrational degrees of freedom, yields:

\[
\lambda = 2.63 \times 10^{-23} \frac{T^{1/2}}{\sigma^2 \Omega_v} M \]

where:

- \( T \): the temperature in K
- \( k \): the Boltzmann constant = 1.3805 \times 10^{-23} J/K
- \( M \): the molecular weight in kg/mol
- \( \sigma \): the characteristic dimension of the molecule in m
- \( \Omega_v \): the collision integral, dimensionless

Eucken [4] proposed some modifications in Eq. (17) to take into account the polyatomic gases by introducing translational and internal degrees of freedom. Generally the methods useful for estimating the pure gas thermal conductivity at atmospheric pressure use a particular so-called Eucken [4] factor \( \lambda M/\mu \) which usually depends upon \( T \), and \( \sigma \); in any case independent values of the gas viscosity and heat capacity are necessary. Some methods require only critical temperature and pressure and are based on the group contribution method in order to take into account the internal degrees of freedom. Summarizing, the Eucken factor should decrease with temperature, but, from experimental measures, in several cases the factor appears to increase. Generally all the proposed methods show errors near 10%.

3.2. The temperature dependence of thermal conductivities of gases at low-pressure

Thermal conductivities of low-pressure gases increase with temperature at low-pressure. The exact function \( \lambda(T) \) is difficult to propose in analogic form: some other temperature-dependent parameters are necessary in the equations. The range of \( d\lambda/dT \) is from 4 \times 10^{-3} to 1.5 \times 10^{-4} W/(m K^2); the complex and polar molecules show the larger values. Some power laws relating \( \lambda \) with \( T \) have been proposed without acceptable results.
3.3. The thermal conductivities of pure gases as function of pressure
The thermal conductivities of all gases increase with pressure, and three regions can be usefully described [4]:

3.3.1. Very Low Pressure
Below about 103 bar (the mean free path of the molecules is comparatively larger with respect to the dimensions of a measuring cell), the gas thermal conductivity can be treated as proportional to the pressure. The term zero-pressure is usually used.

3.3.2. Low Pressure
From about 103 to 10 bar the gas thermal conductivity increases about 1% or less per bar and the 1-bar value or the “zero-pressure” extrapolated value can be used.

3.3.3. High Pressure
The gases thermal conductivity increases with pressure, and close to the critical point the effect of pressure is very high. When the temperature increases at low pressures the gas thermal conductivity becomes larger, but at high pressure the opposite effect is shown. Similar behaviour is evident for the region below $T_c$, where $\lambda$ for liquids decreases with temperature, while for gases there is an increase of $\lambda$ with $T$. Substantially pressure effects are small below $T_c$, exception doing for the behavior of $\lambda$ near the critical point; in this region $\lambda$ can increase by a factor of six (the so-called enhancement in the critical region). This enhancement is bigger for the thermal conductivity with respect to the analogous one evidenced for viscosity.

3.4. Thermal conductivities of gas mixtures
When between the molecules of the mixture there is a great difference in polarity, usually the mixture thermal conductivity is larger with respect to the thermal conductivity predicted from a mole fraction average; for nonpolar molecules, the opposite trend is evident and is very high if the difference in molecular weights or sizes of the constituents is high. It is very difficult to modify monatomic mixture correlations to cover polyatomic molecules. The proposed techniques proposed are essentially empirical and the corresponding states methods for low-pressure were proposed with poor results. Very few experimental data [4] for gas mixtures at high pressures are presented in literature and generally the researches are concerned with simple gases and light hydrocarbons: nitrogen-carbon dioxide, ethylene mixtures with nitrogen and carbon dioxide, rare gases and binaries containing carbon dioxide, nitrogen, and ethane, methane-carbon dioxide and methane-carbon tetra-fluoride binaries. The proposed estimation methods are substantially modifications of procedures developed for low- and high-pressure pure gas thermal conductivities; they are tested by the available experimental data and average errors of about 7% are found.

4. Thermal conductivities of liquids
The thermal conductivities of organic compounds in the liquid phase are usually about 10 to 100 times larger than those of the low-pressure gases at the same temperature. The dependence on pressure is generally small (at pressures less than about 50 bar) and the increase of the temperature produces a decrease of the thermal conductivity. The values of $\lambda$ for the common organic liquids vary in the range 0.100 to 0.200 W/(m·K) at temperatures below the normal boiling point, exception doing for some compounds as for example water, ammonia and other highly polar molecules.

4.1. Thermal conductivity of pure liquids as function of temperature
Almost all estimation methods for pure liquids thermal conductivity are empirical, even if they appear reliable below the normal boiling point. Two methods in particular are selected and tested in [4]:

8
4.1.1. Latini, et al. Method [4,16]
The method of Latini et al is very simple and the suggested correlation is as follows:

$$\lambda = A \frac{(1-T_r)^{0.38}}{T_r^{1/6}}$$

(18)

where:

$$\lambda = \text{liquid thermal conductivity in W/(m K)}$$

$$A = \frac{A^* T_b^\alpha}{M^\beta T_c^\gamma}$$

(19)

$$T_b = \text{normal boiling temperature (at 1 atm), K}$$

$$T_c = \text{critical temperature, K}$$

$$M = \text{molecular weight, g/mol}$$

$$T_r = T/T_c$$

The parameters $A^*$, $\alpha$, $\beta$ and $\gamma$ are proposed for several organic families (Saturated Hydrocarbons, Olefins, Cycloparaffins, Aromatics, Alcohols, Organic Acids, Ketones, Esters, Ethers, Refrigerants); errors are usually less than 10%.

4.1.2. Sastri Method [4]
The Sastri method is represented by the following correlation:

$$\lambda = \lambda_b a^m$$

(20)

where:

$$m = 1 - \left(\frac{1-T_r}{1-T_{br}}\right)^n$$

(21)

$\lambda_b$ is the thermal conductivity at the normal boiling point and is calculated by the group contribution values and corrections; $T_r$ and $T_{br}$ are the reduced temperature and the reduced normal boiling point; for alcohols and phenols $a=0.856$ and $n=1.23$, for other compounds $a=0.16$ and $n=0.2$. Sastri claims an absolute average deviation of 8%.

4.2. Thermal conductivities of pure liquids as function of pressure
At pressures up to 50 to 60 bar, the dependence of the liquid thermal conductivity on the pressure is negligible (exception doing for the range close to the critical point, where the so-called critical enhancement occurs). At lower temperatures $\lambda$ increases with pressure.

A useful way (Lenoir [17]) of estimating the effect of pressure on $\lambda$ is given by the relation:

$$\frac{\lambda_2}{\lambda_1} = \frac{L_2}{L_1}$$

(22)
\( \lambda_2 \) and \( \lambda_1 \) refer to liquid thermal conductivities at \( T \) and pressures \( P_2 \) and \( P_1 \); \( \lambda_2 \) and \( \lambda_1 \) are functions of the reduced temperature and pressure, as shown in particular graphs. A test with experimental data for 12 liquids, both polar and nonpolar, shows errors of only 2% to 4%.

Missenard [18] and Latini and Baroncini [19] proposed other simple correlations extending the calculations to very high pressures.

4.3. Thermal conductivities of liquid mixtures
Several organic liquids mixtures show thermal conductivities generally less than those predicted by a mole or weight fraction average. The methods present in the literature are usually proposed for temperatures near 20°C.

4.3.1. Filippov correlation [20,21]
Filippov proposed the following equation:

\[
\lambda_m = w_1 \lambda_1 + w_2 \lambda_2 - 0.72w_1w_2(\lambda_2 - \lambda_1)
\]  

(23)

where \( w_1 \) and \( w_2 \) are the weight fractions of components 1 and 2; \( \lambda_1 \) and \( \lambda_2 \) are the thermal conductivities of the pure components. Obviously \( \lambda_2 > \lambda_1 \). The constant 0.72 may be adjustable if binary mixture data are available. The correlation is not suitable for multicomponent mixtures.

4.3.2 Jamieson et al. Correlation [22]
Jamieson et al proposed the following equation:

\[
\lambda_m = w_1 \lambda_1 + w_2 \lambda_2 - \alpha(\lambda_2 - \lambda_1)\left[1 - (w_2)^{1/2}\right]w_2
\]  

(24)

where \( w_1 \) and \( w_2 \) are weight fractions and \( \lambda_2 > \lambda_1 \). The parameter \( \alpha \) is equal to unity if mixture data are unavailable. The authors claim an average error within about 7% for all types of binary mixtures. Also in this case the correlation is not suitable for multicomponent mixtures.

4.3.3 Baroncini et al. [23,24,25] correlation
The correlation of Baroncini et al is an extension of eq(18) to binary liquid mixtures and is given by the following equation:

\[
\lambda_m = \left[x_1^2 A_1 + x_2^2 A_2 + 2.2\left(\frac{A_1}{A_2}\right)^{1/2} x_1 x_2\left(1-T_{rm}\right)^{0.38} T_{cm}^{1/6}\right]
\]  

(25)

where \( x_1 \) and \( x_2 \) are the mole fractions of the components 1 and 2. The parameters \( A_1 \) and \( A_2 \) can be estimated from Eq.(19) or can be calculated from pure component thermal conductivities. The mixture reduced temperature is \( T_{rm} = T/T_{cm} \), where:

\[
T_{cm} = x_1 T_{c1} + x_2 T_{c2}
\]  

(26)

with \( T_{c1} \) and \( T_{c2} \) the pure component critical temperatures. The choice between components 1 and 2 is made with the criterion \( A_1 \leq A_2 \). The test of the correlation with over 600 datum points for 50 binary systems including those with highly polar components produced an average error of about 3%. The method is not suitable for multicomponent mixtures.

The methods suggested in this section for estimating \( \lambda_m \) have been tested by binary mixture data, they require the thermal conductivities of the pure components and so they are interpolative in nature.

5. An up-to-date review
In the scientific and technical literature are available a lot of experimental and estimated dynamic viscosity and thermal conductivity data for organic gases and liquids at the atmospheric pressure in the temperature range from the normal freezing point to the normal boiling point (and over) at saturation pressures. A complete and updated source of data can be found in the DIPPR 801 database [26]. For data elaboration a large collection of data is also due to Vargaftik et al [27]. Both the collections are presented with the accuracies for the experimental data; when experimental data are not available, suggested accuracies are presented and often they are greater than 25%. Useful reviews of the researches on thermophysical properties are due to Assael et al [28], Millat et al [29] and Horvath [30].

A last estimation method for liquid thermal conductivity can be considered and is due to Gharagheizi et al [31]: the method is based on a group contribution method and concerns 1635 pure chemical compounds with about 19,000 liquid thermal conductivity data extracted from the DIPPR 801 database at different temperatures. The parameters of the model cover 49 chemical substructures plus temperature. This method is cited for its applicability in terms of number of compounds and large temperature ranges. The authors claim an average absolute relative deviation less than 7.1%.

6. Conclusions
Several techniques to estimate dynamic viscosity and thermal conductivity of fluids [28, 29, 30] have been published including the theoretical and semi-theoretical investigations concerned with the atomic and molecular structure of the different compounds in the gaseous or the liquid phase. In this paper separate sections are presented to describe the more important methods able to estimate with acceptable accuracy dynamic viscosity and thermal conductivity of gases and liquids. These methods, very useful for engineering purposes, are essentially based on group contributions, or on the corresponding stetes principle, or on empirical calculations obtained from the experimental available data. Sometimes it is difficult to realize the difference among these categories, and the distinction is not clear (many methods present both corresponding-states and empirical features). Equations based on group contributions and empirical correlations often lead to big tabulations of constants for individual compounds. The methods adopted for mixtures are often valid at ambient temperature and the lack of experimental data make difficult to known their degree of accuracy. Summarizing, empirical estimation techniques find their greatest applications for low-pressure gas and gaseous mixtures. The dense fluid region is generally described by corresponding-states methods.

7. Nomenclature

| Symbol | Definition                               |
|--------|-----------------------------------------|
| ω      | acentric factor                         |
| T      | absolute temperature, K                 |
| T_c    | critical temperature, K                 |
| T_b    | normal boiling point, K                 |
| T_f    | Normal freezing point, K                |
| P_c    | critical pressure, bar                  |
| V_c    | critical volume, cm³mol⁻¹              |
| T_r    | reduced temperature = T/T_c             |
| M      | molecular weight, g/gmol or kg/kmol    |
| μ      | dynamic viscosity, poise (P)            |
| ν      | Kinematic viscosity, stoke (St)         |

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