To the theory of thermal conductivity of binary liquids

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Abstract. An analytical description of the dependence of the ratio of thermal conductivity of heterogeneous liquids in the form of function on concentration and temperature is given. It has been proven that the main factor that plays a major role in the process of thermal conductivity is the interaction of volume molecules with surface molecules.

1. Introduction
This paper will provide some analytical and experimental results on the dependence of the thermal conductivity ratio \( \frac{\kappa}{g} \) of liquid mixed solutions in the form of function from temperature \( T \) and relative concentration \( \xi = \frac{c}{c_r} \), where \( c \) – concentration of foreign additive mixed with homogeneous composition, \( c_r \) – percolation threshold [1], which is also often referred to as the flow effect. In the first part of the article, we will elaborate on the analytical description of dependency \( \kappa(\xi, T) \) for the simplest case of binary solutions, and then give its generalization in case of an arbitrary number of additives, the concentration of which will be denoted by a dimensionless parameter \( \xi_i \), where index \( i = 1, 2, \ldots, p \), and \( p \) – full amount of additional liquids. As to the physical properties of such heterogeneous mixtures, they are quite understandable and easily explained from the point of view of the basic laws of the theory of heat transfer in heterogeneous structures, detailed, for example, in the monograph [2]. Although this monograph reflects the basic principles of the theory of heat transfer not for liquids, but for heterogeneous crystals, the general physical principle described in it can easily be transferred to liquid mixture solutions. Since there is always a boundary setting when describing the phenomena of heat transfer, the key point of the theory below will be to take into account the connection between volume molecules and surface molecules, which we will consider to be equilibrium when solving the Boltzmann equation. This means that they must have their own temperature equal to the temperature of the thermostat \( T_0 \) and be described as an equilibrium distribution function, as opposed to volumes, which are considered quasi-equilibrium but with temperature \( T \neq T_0 \) (details below). It should be noted that we have not found a solution to the problem, taking into account the phenomenologically introduced additional integral of collisions
associated with the interaction of volume molecules with surface molecules, in the literature known to us on the classical kinetic equation of Boltzmann. The second part of the work will provide the results of experimental measurements of thermal conductivity of liquid mixtures for a fairly wide range of solutions.

2. Description of the thermal conductivity of the mixture solutions
In this section, we will elaborate on the analytical description of the thermal conductivity ratio of liquid solutions, using the basic principles of the theory of nonequilibrium processes [3], [4], and the general positions of the physical properties of surfaces [5]. To this end, it is convenient to take advantage of the principle of additive heat flows for the case of binary liquids, which means equality

\[ q = \sum_{i,k=1}^{2} A_{ik}(\xi)q_{ki} = -\kappa \nabla T, \]  

where \( \kappa \) – the coefficient of thermal conductivity of the solution, \( q_{ki} = -\kappa_{ki} \nabla T \), \( A_{ik}(\xi) \) – matrix function, depending on the concentration \( \xi \) of the liquid added. As has been detailed in [2] the use of quantum theory methods of nonequilibrium processes, based on the Kubo formula, the formula (1) allows us to bring the overall thermal conductivity ratio for the case of binary mixtures to the species

\[ \kappa = (1-\xi)^2 \kappa_{00} + \xi(1-\xi)(\kappa'_{11} + \kappa_{10}) + \xi^2 \kappa_{11}, \]  

where \( \kappa_{00} \) – thermal conductivity of the main liquid, \( \kappa_{11} \) – the thermal conductivity of the liquid added, and the coefficients \( \kappa'_{11} \) and \( \kappa_{10} \) in terms of dimensions correspond to thermal conductivity, but in their physical sense are responsible for heat transfer at the boundary of contact of different phases. In the event that there is no sharp boundary between the contact area of the mixed liquids, the formula (2) is greatly simplified and can be presented in the next very compact form

\[ \kappa = (1-\xi)^2 \kappa_{00} + \xi^2 \kappa_{11}, \]  

where abbreviated designations are introduced \( \kappa_0 = \kappa_{00} \) and \( \kappa_1 = \kappa_{11} \), which correspond to the usual thermal conductivity ratios in the main liquid and in the additive.

Each of these coefficients can be easily assessed on the basis of the classical theory of liquids, using the isotropic gas-kinetic approximation of the thermal conductivity factor, similar to how it was done, for example, in the work of the [2] (compare with with monograph [6]) for diffusion ratios, i.e.

\[ \kappa_{0,1} = \frac{\bar{n}}{3Z_{0,1}} \int \nu^2 \tau_{0,1}(p) \varepsilon_{0,1}(p) \frac{\partial f_{0,1}(p)}{\partial T} d^3 p, \]  

where energy of molecule is \( \varepsilon_{0,1}(p) = \frac{p^2}{2m_{0,1}}, \) \( m_{0,1} \) – respectively, the mass of the molecules of the main liquid and the additive, \( \bar{n} \) – average concentration of volume molecules, \( \tau_{0,1}(p) \) – relaxation time of
molecules in the main fluid and in the additive respectively, \( f_{0,1}(p) = e^{-\frac{p^2}{T_f}} \) – Maxwell's equilibrium distribution function, and \( Z_{0,1} = \int f_{0,1}(p) d^3p \) – ratio multiplier. The permanent Boltzmann \( k_B \) here and everywhere further will be considered equal unit. Using the definition \( p = m v \), after moving to a spherical system of coordinates on momentums, the expression (4) can be rewritten in a simpler form

\[
\kappa = \frac{\bar{n} \int_0^\infty p^2 \tau(p) \overline{f}(p) \, dp}{12m^4 \pi^2 \int_0^\infty p^2 f(p) \, dp},
\]

where mass \( m \) should be understood by mass \( m_{0,1} \). If we now use the medium time and carry out a simple integration on momentums, we will come to the formula

\[
\kappa = \frac{2\bar{n} \pi T_0 \, J_2}{3m \, J_1},
\]

where \( J_1 = \int_0^\infty x^2 e^{-x^2} \, dx = \frac{\sqrt{\pi}}{4} \), \( J_2 = \int_0^\infty x^8 e^{-x^2} \, dx = \frac{105\sqrt{\pi}}{32} \). Substituting the values of these integrals, we come to the final answer

\[
\kappa_{0,1} = \frac{35\bar{n} \pi T_0}{4m_{0,1}},
\]

where the average relaxation time \( \bar{\tau} \) we have to calculate with the help of a simple algorithm, proposed in the work [2]. However, unlike the approach presented in this work, when it comes not to diffusion, but to thermal conductivity, the physical staging here is quite different. Indeed, in the absence of a connection with the thermostat, Boltzmann's kinetic equation for distribution function \( f_p \), where \( p \) – is classical momentum of molecule, we can write in the form (see refs. [7] – [10])

\[
\dot{f}_p = L_0(f_p),
\]

where the collision integral has a classic look

\[
L_0(f_p) = \bar{n} \sum_{p_p, p_p'} \sigma |v - v_p| \left( f_{p_p} f_{p'_p} - f_{p_p} f_{p'_p} \right),
\]

\( \sigma \) – scattering of bulk molecules on top of each other, \( v \) – their speed associated with the momentum of the usual linear ratio \( p = m v \), where \( m \) – is the mass of molecule. As you can see, the equation (7) is written in a purely formal view, which does not take into account (if we are talking about thermal conductivity) the connection with the thermostat. The basic idea of our approach is based on the additional
interaction associated with the connection of volume-based unbalanced molecules with surface fluid molecules, which can automatically be considered a thermostat. They are characterized by an equilibrium distribution function

$$f_p = e^{\frac{\varepsilon_s(p) - \mu}{T_0}}$$

(9)

where the kinetic energy of a single liquid molecule in the surface layer can be represented as a form of

$$\varepsilon_s(p) = \frac{p^2}{2m} - \frac{z\alpha_s}{n_s \delta}$$

(10)

$$\mu_s$$ – is a chemical potential of surface molecules, $$T_0$$ – is a temperature of thermostat and recall that the Boltzmann’s constant $$k_B = 1$$, $$\delta$$ – the thickness of the surface layer, $$\alpha_s$$ – surface tension, whose role in the energy interaction (10) is assigned to the average potential energy of interaction between the closest $$z$$ to each other surface molecules, $$n_s$$ – concentration of surface molecules. With that said, the equation (7) can then be presented in the next additive form

$$\dot{f}_p = L_0(f_{p}) + L_s(f_{p}),$$

(11)

where the second integral collisions, describes the interaction of volume molecules with surface thermostat molecules, and is defined as

$$L_s(f_{p}) = n_s \sum_{p, p', p''} \sigma_s |v - v_i|\left(f_{p'} f_{p''} - f_{p} f_{p'} f_{p''}\right).$$

(12)

Note here that the concentration of surface molecules $$n_s$$ we consider small compared to the concentration of volume molecules. That is, the smallness parameter in our task is the attitude $$\frac{n_s}{n}$$, where $$n_s = \frac{N_s}{V_s}$$, $$N_s$$ – number of molecules in surface volume $$V_s = \Sigma \delta$$, where $$\Sigma$$ – surface area, $$\sigma_s$$ – scattering of volume molecules on surface thermostat molecules. Note also that the thickness $$\delta$$ is dictated by the obvious condition of the possibility to introduce surface tension into consideration $$\alpha_s$$ [11]. It is quite clear that the comparison of both in (11) can be done only in the language of reverse times of relaxation. If for the first part the average time of relaxation $$\overline{\tau}$$, and for the second – $$\overline{\tau}_s$$, it should be considered that increased inequality should be met

$$\frac{1}{\overline{\tau}} \gg \frac{1}{\overline{\tau}_s},$$

(13)
which will be fair in the implementation of inequality $\gamma = \frac{n_2}{n} \ll 1$. Due to inequality (13), the solution of the equation (11) can be searched using the method of successive approximations. Indeed, in the first approximation of the hierarchy of the reverse times (13) we have the right to put the voluminous integral of collisions to zero, that is,

$$L(f_\rho) = 0. \quad (14)$$

Its solution, as it is known (see [12] – [14]) defines a quasi-equilibrium distribution function that can be presented as a

$$f_{0\rho} = e^{-\frac{\varepsilon(p) - \pi}{T}}, \quad (15)$$

where $\bar{\mu}$ – medium chemical potential of 3D molecules, and $T = T(t)$ – their quasi-equilibrium temperature. Substituting a solution (15) in the equation (11), we will have in linear approximation on temperature differences $T - T_0$

$$\left. \frac{\partial f_{0\rho}}{\partial T} \right|_{T=T_0} \tilde{T} = n_\rho \sum_{p, p, p_i} \sigma_s |v - v_i| e^{-\frac{\varepsilon(p) - \pi}{T_0}} e^{-\frac{\varepsilon(p) - \mu_i}{T_0}} - e^{-\frac{\varepsilon(p) - \pi}{T}} e^{-\frac{\varepsilon(p) - \mu_i}{T}} \left( e^{-\frac{\varepsilon(p) - \pi}{T_0}} e^{-\frac{\varepsilon(p) - \mu_i}{T_0}} - 1 \right).$$

Using the law of energy conservation $\varepsilon(p) + \varepsilon(p_i) = \varepsilon(p') + \varepsilon(p_i')$ it follows that

$$\left( \frac{\varepsilon(p) - \bar{\mu}}{T_0^2} \right) \tilde{T} = n_\rho \sum_{p, p, p_i} \sigma_s |v - v_i| e^{-\frac{\varepsilon(p) - \mu_i}{T_0}} \left( e^{-\frac{\varepsilon(p) - \pi}{T_0}} e^{-\frac{1}{T}} - 1 \right) \approx$$

$$\approx n_\rho e^{\mu_i/T_0} \left( T_0 - T \right) \sum_{p, p, p_i} \sigma_s |v - v_i| e^{-\frac{\varepsilon(p) - \mu_i}{T_0}} \left( \varepsilon(p) - \varepsilon(p') \right). \quad (16)$$

So, as it should be (see, for example, [14]), we come to the equation

$$\tilde{T} = -\frac{1}{\tau_s} (T - T_0), \quad (17)$$

where the average time of surface relaxation is introduced due to the ratio
\[
\frac{1}{\tau_s} = \left\langle \frac{1}{\tau_s(p)} \right\rangle = \frac{1}{Z} \int \frac{\mathcal{Z}}{\tau_s(p)} d^3p ,
\]
(18)

and the ration multiplier in the denominator is
\[
Z = \int e^{-\frac{\varepsilon(p) - \varepsilon(0)}{T_0}} d^3p = \frac{\sqrt{\pi}}{4 (2mT_0)^{\frac{3}{2}}} \mathcal{Z} e^{\varepsilon_0} .
\]
(19)

According to (16) for the return time of relaxation you can then write down the following expression
\[
\frac{1}{\tau_s(p)} = \frac{n_s \mu_s}{\varepsilon(p) - \mu} \sum \sigma_s v - v_i | k \frac{\varepsilon(p)}{\mu} \left( \varepsilon(p) - \varepsilon(p') \right) \varepsilon_s(p') .
\]
(20)

The task, therefore, came down to the calculation of the amount in (20). In the work [4], a method of calculating this type of sum by moving to the coordinate system, in which one of the molecules rests, was proposed. However, this assumption is quite small, as it is simply impossible to calculate the amount (20). For this purpose, we have proposed a simple method of transition from summation to integration by presenting the formula (20) in an integral form. Indeed, believing that \( p_i = m v_i = 0 \), we will rewrite the expression (20) in the following form
\[
\frac{1}{\tau_s(p)} = \frac{n_s \sigma_s e^{\varepsilon_0}}{(\varepsilon(p) - \mu)} \int d\varepsilon d^3p' \left\langle \varepsilon(p) - \varepsilon(p') \right\rangle \delta \left( \varepsilon(p) - \varepsilon(p') - \varepsilon_s(p') \right) \delta(p - p' - p') .
\]
(21)

Elementary analysis of the laws of energy and momentum, taking into account dependence (10) suggests that the area of integration by virtual impulses should be clamped by the condition
\[
\sqrt{\frac{p^2}{4} + q - \frac{p}{2}} \leq p' \leq \sqrt{\frac{p^2}{4} + q} .
\]
(22)

where parameter \( q = \frac{mZ\alpha_s}{\mu} \). Thus, taking advantage of the properties of delta - functions and moving to the spherical system coordinates from (20) with account of (22) find
\[
\frac{1}{\tau_s(p)} = \frac{2\pi n_s \sigma_s e^{\varepsilon_0}}{3(\varepsilon(p) - \mu)p} \int_0^r dp' \left\langle \varepsilon(p) - \varepsilon(p') \right\rangle \frac{p}{j} \left( \cos \theta - \frac{p'^2 - m^2}{pp'} \right) \sin \theta d\theta ,
\]
where \( p_i = \sqrt{\frac{p^2}{4} + q - \frac{p}{2}} , \quad p_z = \frac{p}{2} + \sqrt{\frac{p^2}{4} + q} . \)
As a result of simple integration, taking into account the condition of rationing (18), we get in the end

\[ \frac{1}{\tau_s(p)} = \frac{\pi n \sigma e^{\mu_s/q}}{9m^2(e(p) - \bar{\mu})} . \]  

(23)

From what can be seen that another additional condition must be fulfilled, namely the pulse of the volume molecule is subordinated to inequality

\[ p \geq \sqrt{\frac{q}{2}} . \]  

(24)

Before we start calculating the average from the expression (23) according to the definition (17), we need to estimate for the average values of chemical potentials \( \bar{\mu} \) and \( \mu_s \). This is the easiest way to do this if you take advantage of the general definition [15]. Indeed, for the average value of the chemical potential of the liquid we have

\[ \bar{\mu} = \frac{E - T_0 \bar{S}}{N} + P \frac{V}{N} = \bar{\varepsilon} - T_0 \bar{s} + P \, \bar{v} , \]  

(25)

where \( \bar{S} \) — average entropy of molecules ensemble, \( P \) — is a pressure, \( \bar{E} \) — average internal energy of liquid (or gas), \( \bar{\varepsilon} \) — average energy alone molecule, \( \bar{s} \) — average entropy per molecule of liquid, \( \bar{v} \) — volume of one molecule. Calculating the average entropy by the definition given in the monograph [15] already mentioned \( \bar{s} = -\frac{1}{Z} \int f \ln \left( \frac{f}{e} \right) d^3 p \), after a simple integration leads us to such a response

\[ \bar{s} = \frac{7}{2} . \]  

For average energy \( \bar{\varepsilon} = \frac{1}{Z} \int e f d^3 p \) get \( \bar{\varepsilon} = \frac{3T_0}{2} \). Finally, if you use the ideal gas state equation \( PV = NT_0 \), you know, from the formula (25) it follows that

\[ \bar{\mu} \approx -\frac{3T_0}{2} . \]  

(26)

For the chemical potential of surface molecules \( \mu_s \), which also appears in the definition (23), it is necessary to take additional consideration of surface tension \( \alpha_s \). But since surface tension is the potential energy of interacting molecules, this component in the general definition (25) should come in with a "minus" sign. (see ref. [4]). As a result, the formula (25) is easily modified and we get

\[ \mu_s = \bar{\mu} - \frac{\alpha_s}{n_s} . \]  

(27)

The same reasoning that led us to account (26) allows us to rewrite the formula (27) in a rather compact form, as
\[
\mu_s = -\frac{3T_0}{2} - \frac{\alpha_s}{n_s \delta}.
\]  

(28)

So, taking into account (26) and (28) for (23) we get

\[
\frac{1}{\tau_s(p)} = \frac{\pi n_s e^{-\frac{\alpha_s}{n_s \delta} \rho} p \left(2p^2 - q\right)}{9m^2 \left(\varepsilon(p) + \frac{3T_0}{2}\right)}.
\]  

(29)

Averaging a formula (29) on equilibrium distribution function according to (17) and taking into account inequality (24) leads us to the next answer

\[
\frac{1}{\tau} = \frac{4\pi n_s e^{-\frac{2\alpha_s}{n_s T_0}}}{45m^2 T_0 Z} \int \frac{p^3 \left(2p^2 - q\right) e^{-\frac{p^2}{2m T_0}} dp}{\sqrt{\pi}} = \frac{94\sqrt{\pi n_s e^{-\frac{2\alpha_s}{n_s T_0}}}}{45m} (2m T_0)^{\frac{1}{2}} \int_a^\infty x(x-a) e^{-x} dx =
\]

\[
= \frac{94\sqrt{\pi n_s e^{-\frac{2\alpha_s}{n_s T_0}}}}{45m} (2m T_0)^{\frac{1}{2}} (a+2) e^{-a},
\]

where parameter \( a = \frac{z\alpha_s}{4n_s T_0 \delta} \). Or explicitly

\[
\frac{1}{\tau} = \frac{188\sqrt{\pi n_s e^{-\frac{5\alpha_s}{4n_s T_0 \delta}}}}{45m} (2m T_0)^{\frac{1}{2}} \left(1 + \frac{z\alpha_s}{8n_s T_0 \delta}\right).
\]  

(30)

Thus, the average thermal conductivity ratio according to its gas-kinetic representation according to the formula (6) can be recorded as

\[
\kappa = \frac{1575T_0 e^{\frac{5\alpha_s}{4n_s T_0 \delta(T_0)}}}{752\sqrt{\pi} \rho_s (2m T_0)^{\frac{1}{2}} \left(1 + \frac{z\alpha_s}{8n_s T_0 \delta(T_0)}\right)}.
\]  

(31)

Note here that the width of the surface \( \delta \) layer is the most important physical parameter, which determines the entire physics of the processes of heat transfer not only in liquids, but also in solids and, and, in the entire temperature range (from absolute zero to infinity). For water, it can be considered that

\[
\delta(T) = \frac{z\alpha_s}{n_s T}.
\]  

Then from (31) it follows that
\[ \kappa = \frac{1575e^{2}}{846\sqrt{\pi}\sigma_{s}} \sqrt{\frac{T_{0}}{2m}}. \]  

(32)

This dependence is shown in Fig. 1, and it is in full compliance with the experimental results.

Since the surface width \( \delta \) is highly dependent on the type of substance, we put that

\[ \frac{T\delta(T)}{T_{F}\delta} = \ln^{\beta-1}\left(\frac{T}{T_{F}}\right), \]  

(33)

where \( T_{F} = \frac{z\alpha}{n_{0}\delta} \), \( 1 < \beta < 2 \). From the general formula (31) will get that

\[ \kappa = \frac{1575}{752\sqrt{\pi}} \frac{1}{\sigma_{s}} \sqrt{\frac{T}{2m}} \left(1 + \frac{1}{8} \ln^{\beta-1}\left(\frac{T}{T_{F}}\right)\right) \left(\frac{T_{F}}{T}\right)^{\frac{5}{2}\ln^{\beta-1}\left(\frac{T}{T_{F}}\right)}. \]  

(34)

It is worth noting that in the case of liquids, their calculations are quite similar to what they have demonstrated in [4] the use of Boltzmann's classic kinetic equation rather than the quasi-classical approach, as described, for example, in the [2] and [14].

3. **Experimental measurement of dependence** \( \kappa(\xi, T) \)

As the experiment shows (see also [16]) on homogeneous liquids and on binary, the dependence of the thermal conductivity factor on concentration and temperature can be illustrated by figure 1b and figure 1c. The dotted line is an experimental result, and a solid line is a theory according to the general formulae (2), (3). It is worth emphasizing that due to dependence (2) any experimental results associated with finding out the dependence of thermal conductivity on concentration and temperature, well fit within the framework of this common formula, because for some parameters values they characterize growth \( \kappa \) from \( \xi \), and for others – decline \( \kappa \) from \( \xi \). The same applies to temperature dependence \( \kappa \). It should be noted that the times of relaxation \( \tau_{01} \) and \( \tau_{10} \) differ from each other to the extent of the difference in the relationship of masses of colliding molecules \( \frac{m_{0}}{m_{1}} \) and \( \frac{m_{1}}{m_{0}} \) accordingly.
Figure 1. a) Dependence of water thermal conductivity factor on temperature according to the formula (33). b) Chart of thermal conductivity dependence on mix concentration (Toluol ÷ Ethylene glycol). c) Chart of thermal conductivity dependence on mix concentration (Benzol ÷ Tetrachlormethan).

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