REVIEWS

PREDICTION OF THE THERMAL CONDUCTIVITIES OF LIQUIDS*

L. P. Filippov UDC 536.22

The question of predicting the thermal conductivity of liquids is part of the problem of predicting the thermophysical properties of materials and developing methods for evaluating their properties without using empirical information (based on the structural formula of the substance). The successful development of methods for forecasting the thermodynamic properties of unassociated liquids and gases [1, 2] naturally raises the problem of developing methods for performing an a priori calculation of the transport properties, in particular, the thermal conductivity. It must be said that the first approaches to this problem were studied previously in [3], but it is now possible to perform calculations at a higher level — based on determining the laws valid for a wide class of compounds of different nature.

Before proceeding to the exposition of these laws we shall briefly examine the status of methods for calculating the thermal conductivity of liquids.

The lack of clear ideas regarding the mechanism of heat transfer in polyatomic liquids led to attempts to develop purely empirical computational schemes, whose abundance in itself indicates the inadequacy of the results achieved in this manner. In [4] 26 computational methods known to the author were compared. Comparison of the results for 12 materials reveal that for 7 methods the average deviation from the experimental data is greater than 20% (for one method it equals ∿70%), while separate calculations differ by more than a factor of 2. The average error is less than 10% for only one computational method, but this is achieved by a large amount of work. We are talking about the Robbins—Kingry method, examined in [5] as one of three best methods. The method is constructed based on a mass of data for 70 substances, and the computational scheme includes a table containing 28 positions (degrees of freedom), i.e., parameters of purely empirical origin. The ratio of the number of materials to the number of parameters is not much greater than 2, i.e., on the average the thermal conductivity of one substance is found from data for one similar material. Another drawback of this method is correctly pointed out in [5]: the exponent of the reduced temperature, appearing in the formula, changes in a jumplike fashion from 0 to 1 depending on whether or not the density of the material is greater or less than unity (in g/cm^3). In spite of all these contrivances, the computational error of the Robbins-Kingry method is in many cases large.

We shall examine several more works, published recently but not mentioned in [4, 5]. Baroncini et al. [6] proposed the following formula for the thermal conductivity:

$$\lambda = c\frac{T_{\mathrm{boil}}^{6/5}}{M^{1/2}T_c^{1/6}}\,\frac{(1-\tau)^{0,38}}{\tau^{1/6}}, \tag{1}$$

where $\tau = T/T_c$, T_c is the critical temperature, T_{boil} is the normal boiling point, and M is the molar mass. The coefficient c is different for each of the 11 groups of compounds examined, and in addition even the hydrocarbons separate into four separate groups, and in one-half of the cases the power of M also changes (1/2 in (1) is replaced by 1). As we can see, even here the number of degrees of freedom is too large to be able to employ this method with confidence for calculating the thermal conductivity of little-studied materials. In [7] additional parameters and their classification by substances are introduced in order to describe based on (1) the pressure dependence of the thermal conductivity.

---

*Unfortunately the premature death of Lev Petrovich Filippov prevented him from giving a clear substantiation for the estimate of the error in the prediction of the thermal conductivity, but this in no way reduces the great practical value of this work. Editors.

M. V. Lomonosov Moscow State University. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 53, No. 2, pp. 328-338, August, 1987. Original article submitted April 23, 1986.

Unlike the works studied above, in [8] a universal method suitable, in the opinion of the authors, not only for nonmetallic liquids, but for liquid metals also, is discussed. We point out immediately that the thermal conductivity of liquid metals is described here in the traditional manner — estimation through the electrical conductivity based on the Wiedemann–Franz law. As regards the thermal conductivity of nonmetallic liquids, a variant of the well-known Eyring model, corresponding to the idea that the structure of a liquid is microcrystalline, is employed here. The formula presented by the authors for the thermal conductivity contains an undetermined factor and an undetermined function V_s/V — the relative fraction of the volume of the solid microphase. Comparison with experiment was made for liquid argon and nitrogen.

The latest published work [9] is based on the use of the value of the thermal conductivity at the critical point as the normalizing quantity. In spite of the fact that this quantity plays, of course, the role of an adjustable parameter, the fact that the authors understand poorly the specific nature of the behavior of the thermal conductivity in the vicinity of the critical point already gives a basis for ignoring this work. We can add, however, that the formula of the authors, "tied" to two values of the thermal conductivity, is an equation not for the thermal conductivity, but only for its temperature dependence.

We must say that the foreign literature available to us on this question does not make a significant contribution to the development of methods for performing reliable calculations and especially for predicting the thermal conductivity of liquids.

We shall examine a series of studies performed in recent years at the Moscow State University. These studies have two distinguishing features. First, they employ definite ideas regarding the physics of the process of heat transfer — transfer owing to the collective motion of the medium (phonons) is studied [10]. Second, in these studies the distortions introduced into the experiment by the diffusion transfer or thermal radiation in the medium were taken into account and it was possible to use the measurements of the purely molecular thermal conductivity [11], when the radiation mechanism can be neglected.

The development of the ideas of heat transfer in a liquid by means of hyperacoustic wave motions taking into account absorption and scattering by density fluctuations led in [10] to the following formula for the thermal conductivity of liquids:

$$\lambda = \psi k^{1/3}(c_p\rho)^{2/3}u, \tag{2}$$

where k is Boltzmann's constant; u is the velocity of sound (hypersound); c_p is the specific isobaric heat capacity; ρ is the density; and, ψ is a parameter of order unity. It was pointed out in [10] that the formula (2) describes the thermal conductivity of many liquids on the saturation line (with an error of $\sim$10%), if it is assumed that ψ is a common, weak function of the reduced temperature or density. It was found in [12] that for low-atomic materials (liquified inert gases, oxygen, hydrogen) the formula (2) describes at the same time the dependence on the temperature and pressure for $\psi^{-1} = 9/4$.

The formula (2) has the significant drawback that it does not describe the role of isometry, in particular, the change in the thermal conductivity in transferring from normal alkanes to related isomers. To study this role, in [13] an experimental investigation was undertaken, in the course of which the molecular thermal conductivity of 11 branched alkanes was determined at temperatures up to 500 K. At the same time a number of general laws characterizing the change in the thermal conductivity on branching of hydrocarbon chains, in particular, the fact that the ratio of the thermal conductivity of the branched isomer to the thermal conductivity of the normal alkane with the same number of carbon atoms is independent of the temperature, were determined. Analysis of this experimental material in [14] led to the conclusion that no thermodynamic characteristic of a liquid exhibits any significant changes for isomers with the exception of the criterion for thermodynamic similarity [2, 15]. This quantity is fundamental in the prediction scheme based on methods of thermodynamic similarity, and here at least minimal information about it must be given. The similarity parameter enters into the general form of the one-parameter generalized equation of state, valid for the class of normal (nonassociated) liquids:

$$z = \frac{PV}{RT} = F(\varphi, \tau, A), \quad \varphi = V/V_c. \tag{3}$$

All of the standard "scales" of the similarity parameter (Riedel, Pitzer, and Filippov) are based on the dependence of the reduced saturated vapor pressure on the reduced temperature:

$$\pi_s = \pi_s(\tau,\ A) \tag{4}$$

and differ only by the method used to determine A in (4); they are related to one another in a one-to-one fashion [2]. The fact that A plays a significant role in the description of the thermal conductivity of liquids reminds us of Riedel's work [16], where such a dependence was first studied. Unfortunately this interesting work has not been as widely read as it should have been, possibly because of the publication of [17], where it is asserted without proof that Riedel's formula gives an error of up to 40% for hydrocarbons and the one-parameter approach to the description of the properties is criticized and arbitrarily extended to substances which do not belong to the class of normal substances.

The empirical generalization of the data in [14] led to the formula

$$\frac{\lambda}{\lambda^*} = \left(\frac{8.95}{A}\right)^{0,69} \frac{1}{\varphi^2}\left[1 + 20.6\,\frac{(\varphi - \varphi_m)^2}{\varphi}\right], \tag{5}$$

where

$$\lambda^* \equiv \left(\frac{RT_c}{M}\right)^{1/2}\left(\frac{V_c}{N}\right)^{-2/3}$$

is the parametric unit of thermal conductivity; R is the universal gas constant; N is Avogadro's number; ϕ_m is the value of ϕ corresponding to the minimum of the dependence of $\lambda\phi^2$ on ϕ: $\phi_m = 0.351 + 0.156 \lg A$; A is the similarity parameter [2, 15].

The formula (5) is valid for $A \geq 1$, $\phi_m < \phi < 0.5$. In recent years a generalization of this formula was obtained in the form

$$\frac{\lambda}{\lambda^*} = \left(\frac{8.91}{A + 0.3}\right)^{0,776} \frac{1}{\varphi^2} f, \tag{6}$$

where f = 1 for $\varphi < \varphi_m$, $f = 1 + 21\,\frac{\varphi_m(\varphi - \varphi_m)^2}{\varphi}$ for $\varphi > \varphi_m$; $\varphi_m = 0.359 + 0.056 \lg A$.

The formula (6) is valid in the region $A > 0.3$, $\varphi < 0.5$. The role of the parameter A here is very significant: when it decreases from 4 (inert gases) to 0.3 (hexadecane) the factor in (6) varies by a factor of ∿5.

Below we shall examine in detail the results obtained using the formula (6). At this juncture it is timely to raise the question of what are the physical reasons for the appearance of similarity criteria in relations for the thermal conductivity, and whether or not there is a relationship between (6) and the formula (2).

For this it is necessary to interpret the expression for ψ in (2). In accordance with [10]

$$\psi^{-1} = (12\pi)^{1/3}(\alpha T)^{2/3}(3\gamma^2 + 1)^{1/3}(1 + \xi^{1/2})^{1/3}, \tag{7}$$

where α is the coefficient of expansion; $\gamma \cong 1/u^2\ \partial/\partial\rho\ (\rho u^2)$; and, ξ is a parameter whose magnitude is much less than unity. To transform (7) we write γ in the following form:

$$\gamma = 2\Gamma + \frac{1}{3},$$

$$\Gamma \equiv \frac{d\ln(u\rho^{1/3})}{d\ln\rho},$$

where Γ is the thermodynamic Gruneisen parameter: $\Gamma = \alpha u^2/c_p$. The latter parameter can also be written in the form

$$\Gamma\alpha T = \frac{\left[\alpha T\left(\frac{u^2M}{RT}\right)^{1/2}\right]^2}{C_p/R},$$

where C_p is the molar isobaric heat capacity. Next we take into account the empirical relation [15]

$$\alpha T\left(\frac{u^2M}{RT}\right)^{1/2} \approx 2{,}6$$

and the fact that $2\Gamma >> 1/3$. At the same time it follows from (2) that

$$\frac{\lambda}{\lambda^*} = \frac{0.466}{\varphi}\left(\frac{C_p}{R}\right)^{4/3}\left(\frac{Mu^2}{RT}\right)^{1/3}. \tag{8}$$

Similar results are achieved in studying a different but close model, in which only the scattering of carriers by fluctuations is taken into account:

$$\frac{\lambda}{\lambda^*} \sim \left(\frac{C_p}{R}\right)^2\left(\frac{Mu^2}{RT}\right)^{1/3}. \tag{9}$$

For both models heat transfer by high-frequency oscillations – of the order of the maximum Debye frequencies – is most efficient. At such frequencies the viscoelastic relaxation processes are completed, so that the quantity $C_p^\infty = C_p - C_p^i$, where C_p^i is the heat capacity of the internal degrees of freedom, must be regarded as the heat capacity in the formulas under study. This conclusion agrees with the calculations of [18], where the model of heat transfer by collective motions was employed in order to judge the velocity of the propagation of hypersound.

The quantity C_p^∞ can be expressed in terms of the excess heat capacity

$$\Delta C_p = C_p - C_p^0$$

(C_p^0 is the heat capacity of an ideal gas at the same temperature) thus:

$$C_p^\infty = \Delta C_p + \frac{5}{2}R.$$

According to the theory of thermodynamic similarity the excess (configurational) heat capacity of normal liquids for τ = const is a single-valued function of the similarity criterion:

$$\Delta C_p = \Delta C_p(A). \tag{10}$$

The function (10), according to [15], is a strong function. The reason for the appearance of the parameter A in the relations for the thermal conductivity is now clear. It enters through the value of the heat capacity C_p^∞, which depends on the similarity criterion.

For the reduced-volume interval $\phi = 0.33\text{-}0.4$ the empirical relationship between λ/λ^* and the quantity C_p^∞/R has the form:

$$\frac{\lambda}{\lambda^*} = \frac{0.135}{\varphi^2}\left(\frac{C_p^\infty}{R}\right)^{3/2}. \tag{11}$$

The exponent of C_p^∞/R here, as we can see, lies in the range between 4/3 in (8) and 2 in (9). A somewhat modified formula (11) holds in a wider interval of states ($\phi < 0.45$):

$$\frac{\lambda}{\lambda^*} = \frac{0{,}135}{\varphi^2}\left(\frac{C_p^\infty}{R}\right)^{3/2}[1 - 17(\varphi - 0{,}38)^2]. \tag{12}$$

TABLE 1. Examples of Calculations of the Thermal Conductivity of Polar Substances

Substance, temp., K	A	A_0	$\lambda\cdot 10^3$, W/(m·K)		$\lambda/\lambda_{\text{table}}$
			by (6)	by [19]	
CHF_3, 243	1,77		118	97,4	1,21
		2,17	101		1,04
CHF_2Cl, 293	1,91		101	88	1,15
		2,17	91		1,044
CH_2Cl_2, 293	2,01		156	141	1,11
		2,40	138		0,98
C_2H_5Cl, 290	2,2		143	126	1,44
		2,47	127		1,01
Acetone, 293	1,39		222	162	1,37
		2,08	168		1,03
Methyl formeate, 293	1,64		210	188	1,12
		2,07	181		0,96
Methyl butyrate, 293	0,97		174	146	1,19
		1,33	142		0,98

The formulas (11) and (12) from the practical viewpoint are less convenient than (6) (for them information about the heat capacity or the calculation of (10) through the same values of A must be used). Therefore the main attention here is devoted to the relation (6).

As pointed in [14], this relation describes well the thermal conductivity of hydrocarbons, including isomers of alkanes, alkenes, cyclic and aromatic hydrocarbons, liquified inert gases, the simplest inorganic compounds (such as N_2), etc. In studying a large variety of substances there are also cases when appreciable deviations from (6) occur, and they were pointed out previously by Riedel [16]. It is important that all, however slightly noticeable, deviations are in the direction of the computed values of the thermal conductivity which are higher than the experimental values, as if there exists in all substances an additional mechanism for scattering carriers that increases the thermal resistance.

Analysis of a large amount of experimental data enabled establishing an important fact in recent years: the deviation from formulas of the type (6) is significant for polar substances. The relative deviations from (6), it turns out, do not depend on the temperature. For different substances they correlate with the magnitude of the reduced dipole moment. In connection with this it should be pointed out that the existence of a dipole moment leads simultaneously also to lower values of A than for nonpolar compounds with the same structure. According to [1, 2], A is determined uniquely by the effective number of atoms n^* at the periphery of the molecule, and in order to obtain real values of A for polar molecules it is necessary to introduce a correction to A. It turns out that the formula (6), if the value $A = A_0$ (without corrections for polarity) is substituted into it, describes the thermal conductivity of polar compounds. This significant fact is illustrated in Table 1. Table 1 shows how large the deviations from the calculations based on (6) can be for polar substances and how the transition from A to A_0 puts these calculations "in place."

The clarification of the description of the thermal conductivity of polar compounds as a whole has resolved the problem of the method for calculating the thermal conductivity of normal liquids on the saturation line. To check this assertion we performed calculations for the collection of materials chosen in [5] for testing computational methods (excluding associated compounds) (see Table 2). The rms deviation σ of the computed data from the published data equals 3.1%, and the maximum deviation equals 8%. For the same set of substances Missenar's computational method, studied in [5], gives σ = 12%, the maximum deviation equals 22%, and Sato's method gives σ = 13 and 27%, respectively. The best of the methods examined in [5], the Robbins–Kingry method, gave σ = 6% and a maximum deviation of 16%. Thus the computational method which we have proposed gives much higher accuracy in the calculation of absolute values of the thermal conductivity. Table 3 verifies that the formula (6) also reproduces well the temperature dependence of the heat capacity. (As an illustration n-hexane, employed for testing the computational methods in [15], was used.)

TABLE 2. Examples of Calculations of the Thermal Conductivity of a Group of Substances at 293°K (at 230°K for C_3H_8)

Substance	λ^*	$\lambda \cdot 10^3$, W(m·K)		$\delta\lambda/\lambda$, %
		by (6)	by [19–21]	
C_3H_8	7,58	134	133	+1
n-C_5H_{12}	4,99	115	115	0
n-C_6H_{14}	4,23	120	120	0
2-methyl pentane	4,21	110	108	+2
2,3-dimethyl butane	4,29	101	103	—2
n-C_7H_{16}	3,70	124	124	0
n-C_8H_{18}	3,25	126	125	+1
i-H_8H_{18}	3,25	94	95	—1
n-C_9H_{20}	2,91	129	127	+1
n-$C_{10}H_{22}$	2,62	136	136	0
Cyclohexane	5,03	121	121	0
Methyl cyclopentane	4,83	119	120	—1
Benzene	5,91	146	147	—1
Ethyl benzene	4,17	140	131	+7
CCl_4	4,02	92	101	—8
CH_2Cl_2	6,90	139	141	—2
C_2H_5Br	5,38	104	103	+1
C_6H_5Cl	4,66	127	128	—1
C_6H_5I	3,39	97	101	—4
Ethyl acetate	5,04	153	145	+5
Butyl acetate	3,72	144	137	+5
Diethyl ether	5,26	129	133	—3
Acetone	7,54	168	162	+3
Acetaldehyde	10,38	183	186	—2

TABLE 3. Results of Calculations of the Temperature Dependence of the Thermal Conductivity of n-Hexane on the Saturation Line

Temperature, deg K		293	313	333	353	373	393	413	433	453
$\lambda \cdot 10^3$, W/(m·K)	by [20]	119,6	112,6	106,1	99,9	94,1	88,8	83,8	79,2	75,0
	by (6)	119,4	113,0	106,3	99,8	93,9	88,6	83,5	79,0	75,2

The problem of developing methods for calculating the thermal conductivity of nonassociated liquids may be regarded as solved.

The solution of the problem of calculating the thermal conductivity of liquids brings us to the question of predicting this quantity. In [1, 2] it was explained how the fundamental macroscopic parameters V_c, T_c, and A can be determined based on the structural formula of the substance and how a collection of properties of liquids and gases can be found based on this. For completeness we shall present here a condensed exposition of the main stages of prediction (this is worthwhile doing also in order to refine and supplement the information).

The critical volume V_c of polyatomic substances is predicted by summing the increments Δv_i of atoms and groups from Tables 4 and 5: $V_c = \sum_i \Delta v_i$.

To determine the similarity criterion A it is necessary to use its dependence, mentioned above, on the effective number of atoms at the periphery of the molecules n*, A(n*). The values of n* for atoms and groups are given in Table 6. The dependence A(n*) in the latter works is presented in the form of two relations:

$$\lg A = 2.384 - 0.3061 B^{1/\beta}, \tag{13}$$

$$\frac{B - 1.764}{\sqrt{n^*} - 1} = \frac{1}{6.72 + 8.67(\sqrt{n^*} - 1) - 3.91(\sqrt{n^*} - 1)^2 + 0.521(\sqrt{n^*} - 1)^3}. \tag{14}$$

TABLE 4. Increments to the Critical Volume for Alkanes, Alkenes, Their Halogen Derivatives, Aromatic Hydrocarbons, and Simple and Complex Esters

Radical	C	CH	CH_2	CH_3	C_2H_5	C_3H_7	$\underset{\mid\quad\mid}{\overset{\mid\quad\mid}{HC-CH}}$	$\underset{\mid\quad\mid}{\overset{\mid\quad\mid}{-C-CH}}$
ΔV_c, $cm^3/mole$	15,1	35,8	60	73,1	126,5	183,5	65,6	40,8
$CH_2{=}\overset{\mid}{C}H$	$CH_2{-}\underset{\mid}{\overset{\mid}{C}}$	$-\overset{H}{C}{=}\overset{H}{C}-$ in aromatic rings	$\underset{\mid\quad\mid}{\overset{H\quad H}{C{=}C}}$ cis	$\underset{H\quad\mid}{\overset{\mid\quad H}{C{=}C}}$ trans	$\underset{\mid\quad\mid}{\overset{\mid\quad H}{C{=}C}}$ in alkenes and aromatic rings	$\underset{\mid\quad\mid}{\overset{\mid\quad\mid}{C{=}C}}$ in alkenes		
→ 109,2	86,3	86,0	89,7	92,7	68,9	42,1		
$\underset{\mid\quad\mid}{\overset{\mid\quad\mid}{C{=}C}}$ in aromatic rings	—O—	$-\overset{O}{\overset{\|}{C}}-$	$-\overset{O}{\overset{\|}{C}}-O-$	$H\overset{O}{\overset{\|}{C}}-O-$	F	Cl	Br	J
→ 46,8	31	62	81	98,2	32,5	65,6	80,9	102

TABLE 5. Increments to the Critical Volume for Cyclical Hydrocarbons

Rings	ΔV_c, $cm^3/mole$				
	CH_2	CH	C	C_2H_2 cis	C_2H_2 trans
C_3	55,3	39,3	20	74	78,5
C_4	53,3				
C_5	51,5			67,6	75,6
C_6					

TABLE 6. Increments to the Effective Number of Peripheral Atoms

Atom, group	n^*	Atom, group	n^*
F, Cl, Br, I	1	$-CH_2-$ in cyclones	0,85
CH, CH_3	1	$\underset{\mid}{\overset{H}{-C-}}$	
CH_2	1,3	$\underset{\mid}{\overset{\mid}{-C-}}$ in alkenes	0,15
$=CH_2$ in alkenes	1	$-\overset{O}{\overset{\|}{C}}-$	2,3
$=\underset{\mid}{\overset{\mid}{C}}$ in alkenes and aromatic rings	1	—O—	1
$-\underset{\mid}{\overset{H}{C}}$ in aromatic rings	0,85	$\underset{O}{\underset{\|}{HC-}}$	2,3
CF_2 in perfluoroalkanes	1,54		
CF in aromatic rings	1,6		

TABLE 7. Increments to $\sqrt{c}$, $J^{1/2}$·normal $m^3/mole^{1/2}$

Element	$\sqrt{c_i}$	Element	$\sqrt{c_i}$	Element	$\sqrt{c_i}$
He	0,27	F	0,61	In	(6)
Na	0,55	Al	2,7	Sn	4,4
Ar	1,92	Si	2,0	Te	5
Kr	2,78	P	2,7	J	4,9
Xe	4,23	Cl	2,42	Hf	3,5
Rn	5,8	Ge	3	Ta	(5)
H	0,407	As	3,0	Nb	4
B	1,3	Se	3,2	Tl	(6)
C	1,36	Br	3,35	Pb	(4)
C	1,27	Zr	3,6	Bi	6,2
N	1,0	Nb	5,1	U	4,7
O	0,9	Mo	4		

TABLE 8. Results of Prediction of the Thermal Conductivity of Liquids

Substance	Prediction				λ	
	A_0	A	V_c, cm3/mole	T_c, K	by (6)	by [19, 20]
n hexane	1,46	1,46	367	508	119	120
Isooctane	1,42	1,42	474	530	94	95
Methyl cyclopentane	1,87	1,87	318	530	115	120
Ethyl benzene	1,39	1,39	367	644	146	131
C_2H_5Br	2,40	2,33	207	490	101	103
Ethyl ether	1,78	1,73	284	466	127	133
Ethyl acetate	1,57	1,45	281	530	141	145
Acetone	2,70	1,61	208	517	168	162

The parameter B is essentially the similarity criterion, and in fact it is its anamorphism. The quantity B enters into the equation for the orthobaric density [21]

$$\varphi^{-1} = \frac{\rho}{\rho_c} = 1 + B\theta^{\beta} + (B-1)\theta, \quad \theta \equiv 1 - \frac{T}{T_c}, \tag{15}$$

where β = 0.323.

The use of (13) and (14) determines the quantity A_0 – the value of the similarity criterion which would be obtained without corrections for polarity. The latter is introduced as follows:

$$B = B_0 + \frac{1}{10}\,\frac{\mu^2\left(\frac{V_c}{100}\right)}{C},$$

where μ is the dipole moment in Debye units and C is the dispersion interaction constant, also found by summing increments (see below). The incremental (vector) scheme can in principle be employed also to evaluate μ [22]. This is the value of B that must be used to calculate φ based on (15), while the quantity A_0, obtained from (13) for B_0, neglecting μ, as explained above, must be used in the formula (6).

The following relation is used to determine the critical temperature:

$$\frac{T_c^{1/2} V_c 10^{-3}}{C} = 0{,}709 - 0{,}117 \ln A \left(1 + \frac{1}{5} \ln A\right),$$

and in addition C is determined by summing the increments from Table 7 taking into account the corrections for the role of the orientational interaction:

TABLE 9. Results of the Calculation of the Thermal Conductivity of Isobars of n-Hexane ($\lambda \cdot 10^3$ W/(m·K)) (the top line gives the calculation based on (17) and the bottom line shows the data of [20]; P_S is the saturation pressure)

Temp. deg K	P, MPa				Temp. deg K	P, MPa			
	P_s	10	20	30		P_s	10	20	30
293	$\frac{120}{120}$	$\frac{126}{124}$	$\frac{130}{129}$	$\frac{135}{133}$	413	$\frac{84}{84}$	$\frac{92}{92}$	$\frac{99}{99}$	$\frac{105}{104}$
323	$\frac{110}{109}$	$\frac{116}{115}$	$\frac{121}{120}$	$\frac{124}{125}$	433	$\frac{79}{79}$	$\frac{88}{88}$	$\frac{96}{95}$	$\frac{102}{101}$
343	$\frac{103}{103}$	$\frac{110}{109}$	$\frac{116}{115}$	$\frac{121}{119}$	453		$\frac{85}{84}$	$\frac{93}{92}$	$\frac{100}{98}$
373	$\frac{95}{94}$	$\frac{101}{101}$	$\frac{108}{107}$	$\frac{113}{112}$	473		$\frac{81}{81}$	$\frac{91}{89}$	$\frac{97}{95}$
393	$\frac{89}{89}$	$\frac{97}{96}$	$\frac{103}{103}$	$\frac{109}{108}$					

$$\sqrt{C} = \Big(\sum_i \sqrt{c_i}\Big)\left[1 + 0{,}6\,\frac{\mu^4\left(\frac{V\mathrm{c}}{100}\right)^2}{\Big(\sum_i \sqrt{c_i}\Big)^4}\right].$$

Enough information has now been presented in order to determine from the structural formula all parameters necessary for predicting the thermal conductivity. We shall give some examples of predictions. Table 8 gives the results of the prediction of the thermal conductivity of different types of compounds from the collection of substances presented in Table 2 (from one of the groups). It can be verified that the a priori calculations based on the structural formula enable completely reliable determination of the thermal conductivity of representatives of the class of normal liquids.

This analysis referred to states on the saturation line. We shall present a way to extend these methods to a wider range of states.

The approach adopted is based on the law, established by A. S. Predvoditelev [23], according to which the dependence of the thermal conductivity of liquids and compressed gases on the temperature and pressure is described by the dependence of the excess thermal conductivity on the density (volume):

$$\lambda - \lambda_0 = f(\rho), \tag{16}$$

where λ_0 is the thermal conductivity of the rarefied gas (vapor) at the same temperature. A specific form of the formula (16)

$$\lambda - \lambda_0 = D\rho^n$$

is called the Predvoditelev–Vargaftik formula.

In [24] it was pointed out that the formula (2) admits a generalization analogous to (16):

$$\lambda - \lambda_0 = \psi k^{1/3}(c_p\rho)^{2/3}u,$$

and in addition ψ has the same value for normal alkanes.

Further progress in this question was based on the analysis of experimental data on the dependence of the molecular thermal conductivity on the temperature and pressure from [20]. The generalization obtained has the form

$$\frac{\lambda - \lambda_0}{\lambda^*} = \frac{1{,}35}{A^{0{,}458}}\,\frac{1}{\varphi^3}\,[1 + 9(\varphi - 0{,}38)^2]. \tag{17}$$

The quality of the description of the experimental data based on (17) can be judged from Table 9, where the calculations of the molecular thermal conductivity of n-hexane are compared with the experimental results from [20]. For predictive calculations based on (17) the same starting information – the structural formula – is sufficient. It is only necessary to employ the one-parameter equation of state (see [2]).

Methods for calculating the thermal conductivity have now been extended also to the near-critical region of the liquid-vapor system, where, as is well known, there is a strong singularity in the behavior of this quantity, and more or less sharp and high maxima are present (see [25]).

The prediction of the thermal conductivity of pure liquids makes it natural to use the approaches examined above also for predicting the properties of solutions based only on a knowledge of the properties of the components. This question, however, deserves a separate analysis.

LITERATURE CITED

1. L. P. Filippov, Inzh.-Fiz. Zh., 44, No. 5, 839-856 (1983).
2. L. P. Filippov, Law of Corresponding States [in Russian], Moscow (1983).
3. L. P. Filippov, Reviews of the Thermophysical Properties of Materials [in Russian], No. 2, Moscow (1977).
4. G. Latini and M. Pacetti, Bull. Inst. Int. Froid/Bull. Int. Inst. Refrig., 6, 1-29 (1977).
5. R. Reed, J. Prausnitz, and T. Sherwood, Properties of Gases and Liquids [Russian translation], Leningrad (1982).
6. C. Baroncini, P. Filippo, G. Latini, and M. Pacetti, Int. J. Thermophysics, 2, No. 1, 21-38 (1981).
7. G. Latini and C. Baroncini, High Temp.–High Press., 15, 407-411 (1983).
8. M. P. Saxena, Prabhuram, Thermal Conductivity of Liquids. Them. Cond., New York (1983), Vol. 17, pp. 241-249.
9. T. A. Herrick and J. Lielmers, Thermochimica Acta, 84, 41-55 (1985).
10. L. P. Filippov, Investigation of the Thermal Conductivity of Liquids [in Russian], Moscow (1970).
11. L. P. Filippov, Measurements of the Thermophysical Properties of Materials by the Method of Periodic Heating [in Russian], Moscow (1964).
12. V. M. Shul'ga, "Compensation method of periodic heating for measuring the thermal properties of liquids in a wide temperature range at pressures up to 1000 MPa," Author's Abstract of Candidate's Dissertation, Engineering Sciences, Moscow (1985).
13. L. P. Filippov and L. A. Laushkina, Zh. Fiz. Khim., 58, No. 5, 1068-1071 (1984).
14. L. P. Filippov and L. A. Laushkina, Zh. Fiz. Khim., 58, No. 5, 1078-1082 (1984).
15. L. P. Filippov, Similarity of the Properties of Materials [in Russian], Moscow (1978).
16. L. Riedel, Chemie-Ing.-Techn., No. 4, 209-213 (1955).
17. M. Schneider, Luft und Kaltetechnik, No. 2, 84-88 (1971).
18. R. E. Nettelton, Phys. Fluids, 2, No. 3, 256-283 (1959).
19. N. B. Vargaftik, L. P. Filippov, and A. A. Tarzimanov, Thermal Conductivity of Liquids and Gases [in Russian], Moscow (1978).
20. S. N. Kravchun, "Investigation of the thermophysical properties of liquids by the method of periodic heating," Author's Abstract of Candidate's Dissertation, Physical-Mathematical Sciences, Moscow (1983).
21. L. P. Filippov, Teplofiz. Vys. Temp., 22, No. 4, 679-685 (1984).
22. R. Kreman and M. Pestemer, Dependence between the Physical Properties and Chemical Structure [in Russian], Moscow (1939).
23. A. S. Predvoditelev, Collection of Papers in Honor of Academician P. P. Lazarev [in Russian], Moscow (1956), pp. 84-112.
24. L. P. Filippov and S. N. Kravchun, Izv. Vyssh. Uchebn. Zaved., Neft' Gaz, No. 5, 88-90 (1983).
25. L. P. Filippov, Teploenergetika, No. 5, 10-14 (1986).