Thermal kinetic energy of liquids with conformationally rigid molecules

M.Yu. Gorbachev[a]

[a] Institute of Chemistry, Academy of Sciences, Kishinev MD 2028, Republic of Moldava

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M. YU. GORBACHEV*

Institute of Chemistry, Academy of Sciences, Academic, 3, Str.,
Kishinev MD 2028, Republic of Moldava

It is shown that the thermal kinetic energy of liquids with conformationally rigid molecules can be properly described by means of the two equations. One of them is a new functional dependence of the given quantity on surface tension and molar volume of these liquids. Another one is some linear function between this energy and absolute temperature. The joint use of both these equations allows one to calculate the surface tension of the above liquids.

Keywords: Thermal kinetic energy; Liquids; Conformationally rigid molecules

1. Introduction

Because of different values of their one-particle kinetic energy all the molecules, forming the liquid phase of any chemical compound, can be divided into two groups [1]. The first group contains the so-called 'hot' molecules, whose kinetic energy is greater than or equal to some critical value $-E$ and, therefore, is high enough for their spatial translations. These translations are realized in the form of irregular one-particle jumpings. The molecules of the second group are situated in their potential wells which are caused by the intermolecular attractive forces, existing between these molecules. Thus, the latter molecules take part in their vibrational motion. The relative share of the molecules of both these groups depends on absolute temperature – T.

If the relative share of the molecules, belonging to the first group, equals z, then that of the second one will be: $1 - z$. Any increase in T (and, therefore, in thermal kinetic energy – K of a liquid) will lead to a corresponding increase in z. In turn, the value of z may be easily found by means of Boltzmann statistics (see [1]):

$$z = \exp\left(\frac{-E}{kT}\right), \tag{1}$$

*E-mail: myugorbachev@yahoo.com

where k is Boltzmann constant and E is the above-mentioned critical value of one-particle energy.

Based on consideration of the investigated molecules as some spherical particles, whose effective radius is proportional to $V^{1/3}$ (where V is molar volume of a liquid), it has been shown in the works [2,3] that the following equation holds for the quantity E:

$$E = f\sigma V^{2/3}. \tag{2}$$

In equation (2) σ denotes the surface tension of a liquid; f is some coefficient of proportionality which is constant for various liquids considered at different temperatures.

The joint use of equations (1) and (2) leads to the following expression for the quantity z:

$$z = \exp\left(\frac{-g\sigma V^{2/3}}{T}\right), \tag{3}$$

where g is a constant, whose numerical value is equal to 9.35×10^6 $(\mathrm{J}^{-1}\,\mathrm{K}\,\mathrm{mol}^{2/3})$ for various liquids (see [2,3]).

It has also been shown in [2] that both the above-mentioned relative shares: z and $1 - z$ describe the process of kinetic energy transfer connected with frictional flow of liquids. This fact indicates that these quantities are important for the adequate description of the quantity K.

Bearing in mind all the above reasons, the aim of the present work consist in finding an equation which connects the quantity K with the mentioned shares of the jumping and vibrating molecules of the liquid phase under investigation.

2. Theory

In order to find the above equation let us consider one mole of a liquid with conformationally rigid molecules. We suppose the given liquid is in thermal equilibrium with its saturated vapour (at some fixed absolute temperature – T). Further, we shall consider all the molecules of the investigated liquid phase as spherical particles (hard spheres) due to their fast mutual reorientations. The above value of T is supposed to be high enough for such a consideration to be valid.

The numbers of the jumping and vibrating molecules of the given liquid will be equal to zN and $(1 - z)N$ respectively, where N is Avogadro's number.

Here it is to be noted that we consider the investigated liquid far from its normal boiling point. In this case the vapour microcavities (microbubbles) which are usual for the whole volume of any near-boiling liquid (see [1]) do not exist. Therefore, these microcavities cannot influence the distribution of kinetic energy between the jumping and vibrating molecules of the liquid under consideration.

As the conformationally rigid molecules of the investigated liquid phase are being considered as hard spheres, so hereafter we neglect any intra-molecular motion therein.

Based on this reasoning we may write the following equality for the molar thermal kinetic energy – K_m of the investigated liquid:

$$K_m = I + J, \tag{4}$$

where I is the thermal kinetic energy of its vibrating molecules; and J is that of its jumping ones.

Further, we shall consider all the vibrating molecules as some harmonic three-dimensional oscillators, whose frequency is the same for any vibrational degree of freedom. Then their one-particle time average potential energy – u caused by their intermolecular attraction will be also the same for each of the three vibrational degrees of freedom of any of these oscillators. As has been shown in [2] and [3] the quantity u is some constant share of the above-mentioned critical energy – E:

$$u = \alpha E, \tag{5}$$

where α is the coefficient of proportionality which is constant for various liquids considered at different temperatures.

Here it is to be noted that for harmonic oscillators their above-mentioned quantity u is equal to their one-particle time average kinetic energy for any of their vibrational degrees of freedom [1]. Thus taking into account that the vibrations of the investigated molecules are three-dimensional, and their kinetic energy is evenly distributed [1], we can consider that the average one-particle kinetic energy equals $3\alpha E$ for all the vibrating molecules.

In order to evaluate the average one-particle kinetic energy of the jumping molecules we must take into account that these molecules can abandon the investigated liquid and, therefore, the given molecules are in the state of interphase equilibrium exchange with the molecules of this liquid which form its saturated vapour phase above its surface. Further, supposing that the given vapour phase obeys the perfect gas law and bearing in mind the above reasons, we can consider that the average value of the one-particle kinetic energy of the jumping molecules is equal to $3kT/2$.

Now, using equation (2), the numbers of the jumping molecules and the vibrating ones: zN and $(1-z)N$ respectively side by side with the above-mentioned values of their one-particle kinetic energy, we can write equation (4) in the following form:

$$K_m = 3N\alpha f\sigma V^{2/3}(1-z) + 3kNTz/2. \tag{6}$$

Uniting all the constants of equation (6), we have the following final equation for the molar thermal kinetic energy – K_m:

$$K_m = \delta\sigma V^{2/3}(1-z) + 3RTz/2, \tag{7}$$

where R is the gas constant and δ is some coefficient of proportionality which is constant for various liquids. The value of δ does not depend on T. The given property of δ is caused by the fact that the constants f and α in equations (2) and (5) respectively do not depend on T (see [2,3]). In its turn, the quantity z in equation (7) is defined by means of equation (3).

3. Results and discussion

The practical usage of equation (7) for the calculation of K_m requires the numerical value of constant δ. Its value can be found on the basis of the following reasoning. As the quantity K_m describes the molar thermal kinetic energy of the liquid phase, so its value must remain constant for one mole of different liquids considered at the same temperature. In this case the quantities $\sigma V^{2/3}(1-z)$ and $3RTz/2$ in equation (7) will be connected by some linear dependence which follows from equation (7), when K_m is constant.

In order to evaluate the constant δ the fifteen liquids presented in table 1 were investigated at $T = 293.15\,K$. The values of their quantities V and σ at this temperature were taken from [4–11] side by side with the following numerical value of the gas constant R: 8.3144 (J mol^{-1} K^{-1}) [4]. Here it is to be noted that the compounds given in table 1 were chosen because of the following reasons: firstly, they are well studied experimentally; secondly, their chemical structures differ significantly. A part of them belongs to organic compounds; another part is represented by inorganic substances. The numerical values of δ and K_m defined by the least-squares method applied to the data set of table 1 are 1.4394×10^7 (mol$^{-1/3}$) and 1280.80 (J mol^{-1}) respectively. The data presented in the last column of table 1 show that the quantity K_m remains practically constant for all the investigated liquids.

Further, as K_m is the molar thermal kinetic energy, so this quantity must be some linear function T:

$$K_m = \gamma T + \xi, \tag{8}$$

wherey γ and ξ are some constants which do not depend on the nature of the liquid phase. In order to evaluate both these constants and, therefore, to establish the above linear dependence of K_m on T the twenty eight liquids presented in table 2 were investigated. The values of their quantities V and σ considered at different

Table 1. Towards the evaluation of the quantities δ and K_m at $T = 293.15\,K$.

No.	Compound	$V \times 10^6$ (m^3 mol^{-1})	$\sigma \times 10^3$ (N m^{-1})	$\sigma V^{2/3}(1-z) \times 10^7$ (J mol$^{-2/3}$)	$3RTz/2$ (J mol^{-1})	K_m (J mol^{-1})
1	Benzene[a]	88.9	28.88	483.4221	583.6773	1279.52
2	Bromine	51.2	41.86	485.5990	580.1127	1279.08
3	Carbon diselenide	63.7	36.24	486.5564	578.5515	1278.90
4	Carbon tetrachloride	96.4	26.90	472.4197	602.0417	1282.04
5	Chromyl chloride	80.3	36.44	600.2840	420.2592	1284.31
6	Dibromomethane	69.5	39.79	593.8912	427.8857	1282.73
7	Fluorobenzene	93.9	27.26	469.7216	606.6337	1282.75
8	Phosphorus oxychloride	91.5	32.10	570.2890	457.2402	1278.11
9	Phosphorus(III) chloride	87.5	28.61	470.5352	605.2444	1282.53
10	Pyridine	80.6	35.55	583.3645	440.7404	1280.44
11	Selenophene	85.3	30.10	492.4954	568.9654	1277.86
12	Sulfuryl chloride	81.3	29.44	457.6523	627.6267	1286.37
13	Thionyl chloride	72.7	32.27	488.2605	575.7839	1278.59
14	Thiophene	79.0	31.34	485.4046	580.4307	1279.12
15	Tin(IV) chloride	116.8	27.66	580.6276	444.1442	1279.90

[a] Hereafter all the investigated liquids are at the pressure $P = 0.1\,MPa$.

Table 2. To the definition of the linear dependence of K_m on T.

No.	Compound	T (K)	$V \times 10^6$ $(\mathrm{m^3\,mol^{-1}})$	$\sigma \times 10^3$ $(\mathrm{N\,m^{-1}})$	K_m $(\mathrm{J\,mol^{-1}})$ Equation (7)	Equation (8)
1	Helium	3.05	28.49	0.224	21.47	21.42
2	Hydrogen	16.5	26.89	2.57	79.90	79.81
3	Deuterium	20.0	23.38	3.567	95.04	95.01
4	Nitrogen	65.0	32.62	11.71	286.46	290.37
5	Oxygen	65.0	25.67	19.59	294.05	
6	Fluorine	65.0	23.48	18.95	286.46	
7	Carbon tetrafluoride	110.0	49.2	19.00	482.10	485.73
8	Diborane	130.0	56.3	21.72	576.37	572.56
		150.0	58.9	18.42	659.75	659.39
9	Perchloryl fluoride	193.15	56.3	24.72	847.91	846.72
10	Chlorine	193.15	42.3	34.20	840.35	
11	Propadiene	193.15	55.9	26.64	841.13	
12	Carbon disulfide	253.15	57.6	38.65	1106.58	1107.20
13	Furan	253.15	68.6	29.86	1104.14	
14	Bromobenzene	333.15	109.2	31.18	1449.22	1454.52
15	1,2-Dichlorobenzene	333.15	116.8	31.68	1455.88	
16	1,3-Dichlorobenzene	333.15	118.5	31.42	1456.13	
17	1,4-Dichlorobenzene	333.15	118.4	29.39	1449.05	
18	Arsenic(III) chloride	333.15	87.4	35.80	1448.94	
19	Osmium tetroxide	333.15	60.0	47.00	1449.79	
20	Phosphorus sulfochloride	333.15	107.9	29.37	1451.74	
21	Silicon(IV) bromine	333.15	130.0	25.68	1452.97	
22	Vanadium(IV) chloride	333.15	108.4	32.99	1454.31	
23	Quinoline	423.15	131.1	31.47	1851.83	1845.24
24	Antimony(III) chloride	423.15	91.1	41.24	1845.92	
25	Arsenic(III) bromide	423.15	102.2	38.87	1843.25	
26	Titanium(IV) bromide	423.15	135.9	30.91	1850.38	
27	Antimony(III) bromide	473.15	102.4	43.88	2059.67	2062.31
28	Phosphorus(III) iodide	533.15	117.9	44.06	2324.30	2322.80

temperatures were taken from [4–8,10,12–14]. The given experimental values of V and σ were used in equation (7) in order to calculate the corresponding values of the quantity K_m which, in their turn, are presented in the last but one column of table 2. The evaluation of γ and ξ was done on the basis of the last-squares method applied to the data set of table 2, including the above-mentioned value of K_m at $T = 293.15\,\mathrm{K}$. The numerical values of γ and ξ found in this way are equal to 4.3414 $(\mathrm{J\,mol^{-1}K^{-1}})$ and 8.1792 $(\mathrm{J\,mol^{-1}})$ respectively.

The results of the use of the above values of γ and ξ in equation (8) are presented in the last column of table 2. The comparison of the values of K_m calculated by means of equations (7) and (8) shows that equation (8) allows one to describe the quantity K_m at different temperature as well as equation (7) does (see table 2). Thus, the quantity K_m really depends on T linearly. Therefore, for different liquids both the equations: equations (7) and (8) describe the same quantity: their molar thermal kinetic energy. Based on this conclusion, one can consider that within the framework of the used approximation of hard spheres the quantity ξ in equation (8) is the molar zero-point energy, whose above numerical value is very important for the description of K_m of the following low-temperature liquids: He, H_2 and D_2 (see table 2).

Here it is to be noted that in the common case equation (7) (unlike equation (8)) has the above-mentioned high-temperature limit of its use for the description of K_m of any liquid under investigation. The given limit is caused by the vapour microcavities which

Table 3.   The values of K_m calculated by means of equations (7) and (8) applied to
the liquid range of bromine.

T (K)	$V \times 10^6$ (m^3 mol^{-1})	$\sigma \times 10^3$ (N m^{-1})	T/T_b	K_m (J mol^{-1})	
				Equation (7)	Equation (8)
265.90	49.7	46.82	0.800	1170.79	1162.56
268.15	49.8	46.41	0.807	1177.19	1172.33
273.15	50.1	45.50	0.822	1193.14	1194.03
278.15	50.4	44.59	0.837	1211.20	1215.74
283.15	50.7	43.68	0.852	1231.46	1237.45
288.15	50.9	42.77	0.867	1254.08	1259.15
293.15	51.2	41.86	0.882	1279.08	1280.86
298.15	51.5	40.95	0.897	1306.55	1302.57
303.15	51.8	40.04	0.912	1336.57	1324.27
308.15	52.1	39.13	0.927	1369.23	1345.98
313.15	52.4	38.22	0.942	1404.61	1367.69
318.15	52.7	37.31	0.957	1442.81	1389.40
323.15	53.0	36.40	0.972	1483.90	1411.10
328.15	53.4	35.49	0.987	1527.24	1432.81
332.35	53.6	34.73	1.000	1566.93	1451.04

exist in any liquid considered near its boiling point (see above). All the above-mentioned can be illustrated by means of the calculational data presented in table 3. These data describe the results of the study of the joint use of equations (7) and (8) at different temperatures. The liquid range of bromine is used as an example. The experimental values of σ and V needed for the use of equation (7) were taken from [4,5,7]. The comparison of the values of K_m calculated by means of equations (7) and (8) shows (see table 3) that both these equations lead to the practically equal values of K_m, when the considered values of T are less than $0.91T_b$. (Hereafter for any investigated liquid T_b means its normal boiling point). For the temperature range of bromine which obeys the above condition the absolute value (module) of the relative difference between the values of K_m calculated by means of equations (7) and (8) is less than 1%.

Here it is to be noted that all the liquids presented in tables 1 and 2 are considered at the temperatures which do not exceed $0.91T_b$. Thus, if the temperature of the investigated liquid phase is less than $0.91T_b$, then equations (7) and (8) describe its molar thermal kinetic energy – K_m equally well.

Based on this conclusion, we may combine equation (7) with equation (8). In this case combine these equations lead to the following equation:

$$\delta\sigma V^{2/3}(1 - z) + 3RTz/2 = \gamma T + \xi, \tag{9}$$

which holds over the above-mentioned temperature range.

As the quantity z is defined by equation (3), so equation (9) describes some transcendental dependence of σ on T and V. In this case the quantity σ cannot be expressed in the form of some explicit function of the variables T and V. Nevertheless, equation (9) can be easily solved numerically. The results of this numerical solution are presented in table 4 which describes the calculation of σ for some liquids considered near their chilling points. The experimental values of V and T need for the given calculation were taken from [4,6,7,13]. The comparison of the values of σ calculated by means

Table 4. The values of σ calculated by means of equation (9) for some liquids.

No.	Compound	T (K)	$V \times 10^6$ $(m^3 mol^{-1})$	$\sigma \times 10^3 (N m^{-1})$ Calc.	Exper.
1	Neon	24.55	16.17	5.82	5.68
2	Phosphine	139.40	41.3	27.67	27.44
3	Boron trifluoride	144.79	38.2	23.74	23.14
4	Propyne	170.45	52.2	28.56	29.73
5	Hydrogen sulfide	187.61	34.8	33.32	33.72
6	Hydrogen selenide	207.43	39.6	34.02	34.66
7	Water	273.15	18.02	76.95	75.83
8	Iodine(V) fluoride	282.55	68.0	32.90	31.92
9	1,2-Dibromoethane	282.94	84.7	33.35	34.03
10	Pyrimidine	294.15	78.8	31.11	30.73
11	1,1,2,2-Tetrachlorodifluoroethane	299.15	123.9	23.42	23.18
12	Mercury(II) bromide	514.0	70.5	60.23	61.97

of equation (9) and the corresponding experimental ones taken from [4,7,10,13] shows that equation (9) allows one to calculate the quantity σ usefully. For the compounds presented in table 4 the average absolute value (module) of the relative calculational error of equation (9) is equal to 2.0%.

The calculational data presented in table 4 shows that equation (9) fits for the associated liquids such as: water, mercury(II) bromide, iodine(V) fluoride and boron trifluoride. This fact indicates that, as the jumping molecules of these liquids are practically nonbonded, so the influence of the association of their vibrating molecules on the quantity K_m can be properly taken into account by means of the quantity $\sigma V^{2/3}$ (see the first addendum and the quantity z in equation (9)).

Some of the calculational data of table 4 show that equation (9) may be used for the liquids, whose molecules cannot have their intramolecular conformational transitions within the investigated low-temperature region. So, for instance, in the case of 1,2-dibromoethane and 1,1,2,2-tetrachlorodifluoroethane their molecules are conformationally rigid near the chillings point of these liquids (see [15,16]). Therefore, both these liquids obey equation (9) at the above temperatures (see table 4).

Here it is to be noted that in the common case equation (7) (and, therefore, equation (9)) may have some low-temperature limit of their use. This takes place, when the form of the molecules of the investigated liquid phase is far from spherical and at the same time its temperature is low enough. In this case we cannot consider the above molecules as some spherical particles.

Let us consider an example. The liquid phase of carbon disulfide is built from molecules which are linear [6]. At $T = 230.0$ K the corresponding liquid phase of carbon disulfide has the following values of V and σ: $52.6 \times 10^{-6} (m^3 mol^{-1})$ and $42.35 \times 10^{-3} (N m^{-1})$ respectively [7,14]. The value of K_m calculated by means of equations (7) and (8) are equal to 1052.28 and 1006.70 (J mol^{-1}) respectively. At the same time, when $T = 253.15$ K, both these equations lead to the values of K_m which are practically equal (see table 2). Thus, in the case of carbon disulfide the above-mentioned low-temperature limit of the use of equation (7) is within 230.0–253.15 K. However, for some liquids this low-temperature limit can coincide with their chilling points (see, for instance, the liquids presented in table 4).

4. Conclusion

The following conclusions may be drawn. For various liquids with conformationally rigid molecules equations (7) and (8) allow one to perform the calculation of their molar thermal kinetic energy at temperatures whose values are high enough in order to consider their molecules as spherical particles but are not greater than $0.91T_b$. Within the above temperature range equation (9) can be used for the definition of the surface tension σ of these liquids.

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