Energy of intermolecular forces in liquid halogenalkanes and their binary mixtures

Yu A Neruchev, V I Korotkovskii, O S Ryshkova
Kursk State University, Radischeva, 33, Kursk, 305000, Russia
E-mail: yuan2003@mail.ru

Abstract. The paper analyzes the relation that allows studying the peculiarities of intermolecular forces and the nature of the structure of condensed substances with an atom–atom interaction mechanism. The estimate of the energy of intermolecular forces of saturated hydrocarbons and their halogen-substituted according to the data on their thermophysical properties and data on the individual characteristics of atomic centers are presented. A formula for predicting the dispersion constants of halogen-alkanes and their binary mixtures that accordance with experimental data is proposed.

1. Introduction
The analysis of the known ratios of statistical thermodynamics [1] leads to the conclusion that for the system of interacting atomic centers the relation is valid:

\[ T \left( \frac{\partial p}{\partial T} \right)_V = -\frac{E_p}{V} + \frac{NkT}{V}. \] (1)

From this relation, it follows that the full pressure in the system of interacting atomic centers is determined by the interaction energy density and the particle momentum density. It does not contain empirical parameters and, because of this, can be used to study the nature of intermolecular forces and the level of discreteness in the liquid on the data about the thermophysical properties of substance.

The main advantage of the equation (1) is that the full pressure in it is determined by the sum, and not the difference of the two terms, as is the case in equations like the van-der-Waals equation, which characterizing hydrostatic pressure. This structure of the equation provides a significantly higher accuracy of describing the thermophysical properties with the same initial data and the same models used.

2. Main constants of intermolecular forces
These conclusions confirm the results of experimental studies of the thermophysical properties of liquid hydrocarbons and their halogen-substituted on a liquid-vapor equilibrium curves in a wide range of state parameters, performed in the Laboratory of Molecular Acoustics of the Research Center for Condensed Matter Physics of Kursk State University. In [1–4], it was shown that dispersion attractive forces dominate in liquid hydrocarbons, whose energy is proportional to the square of the substance density. But the key condition for an adequate description of the thermophysical properties in all the entire range of state parameters is to take into account the
far-range binding forces responsible for the association of particles. The constants of dispersion forces $B$ and far-range binding ones $b$ are determined by the critical parameters of a substance according to the formulas:

$$
\left( \frac{\partial p}{\partial T} \right)_V^{\text{cr}} = \frac{B_\rho^3}{T_\text{cr}} + \frac{R}{M} \rho_\text{cr}, \quad (2)
$$

$$
b \approx \frac{RT_\text{cr}}{2M \sqrt[3]{\rho_\text{cr}}}. \quad (3)
$$

Accounting for these forces allows us to estimate the energy of intermolecular forces in a molecular liquid near the melting points:

$$
|E_p| = B \rho^2 + b \rho^{4/3} \left[ 1 - \left( \frac{\rho}{\rho_b} \right)^{11/3} \right]. \quad (4)
$$

Equation (4) takes into account contributions to the intermolecular energy of interactions of those three types of forces: 1) the dispersion forces of attraction ($m = 6$) $E_d = -B \rho^2$, 2) the repulsive forces ($n = 12$) $E_r = +a \rho^4$, and 3) the long-range binding forces ($k = 1$) $E_b = -b \rho^{1/3}$.

The results of calculation of the intermolecular energy for the liquid n-heptane with the help equation (4) and their comparison with the NIST data are given in table 1. For n-heptane, $B = 0.765$, $b = 3637$, $\rho_b = 612.22$ kg/m$^3$ ($\rho_b$ is the density at the boiling point).

From the obtained results, it follows that the main contribution into the energy of intermolecular forces is made by the dispersive attractive forces. The contribution of other forces is the most noticeable near the melting point.

**Table 1.** Intermolecular energy for the liquid n-heptane.

| $t$, °C | $E$, kJ/kg | Err, % | $t$, °C | $E$, kJ/kg | Err, % |
|--------|------------|--------|--------|------------|--------|
|        | $E_{(4)}$  | NIST   |        | $E_{(4)}$  | NIST   |
| −90    | 415.0      | 425.5  | 2.5    | 10         | 348.8  | 351.0 | 0.6 |
| −80    | 408.2      | 417.4  | 2.2    | 20         | 342.2  | 344.0 | 0.5 |
| −70    | 401.5      | 409.4  | 1.9    | 30         | 335.6  | 337.1 | 0.4 |
| −60    | 394.8      | 401.7  | 1.7    | 40         | 328.9  | 330.1 | 0.4 |
| −50    | 388.1      | 394.1  | 1.5    | 50         | 322.2  | 323.1 | 0.3 |
| −40    | 381.6      | 386.6  | 1.3    | 60         | 315.4  | 316.0 | 0.2 |
| −30    | 375.0      | 379.3  | 1.1    | 70         | 308.6  | 308.9 | 0.1 |
| −20    | 368.4      | 372.1  | 1.0    | 80         | 301.6  | 301.6 | 0.0 |
| −10    | 361.9      | 365.0  | 0.9    | 90         | 294.6  | 294.2 | −0.1 |
| 0      | 355.3      | 358.0  | 0.7    | 100        | 287.4  | 286.6 | −0.3 |

To verify adequacy of the above ratios, the authors of [3, 4] performed experimental studies of a large number of saturated hydrocarbons and their halogen-substituted ones. In the range of 25–150°C, at the saturation line and at atmospheric pressure in the without dispersed region on a frequency of 1 MHz speed of sound (0.1%), density (0.05%) and isobaric heat capacity (2%) were measured. Measurements of the isobaric heat capacity were carried out by the method of monotonic heating according to the method [2, 4].

The obtained experimental data were used to calculate the thermophysical properties of the investigated substances, in particular, to estimate the energy of intermolecular forces. In addition to one-component systems, their binary mixtures were also investigated.
As a result, it is shown that dispersion forces make the dominant contribution to the energy of intermolecular forces in liquid hydrocarbons and their halogen-substituted compounds. The constants of the dispersion forces of binary mixtures of n-alkanes with n-alkyls $B_m$ and the constants of n-alkanes dispersion forces $B_n$ are connected by the relation:

$$B_m = B_n \left( \frac{(1 - \chi)\mu_\ell + \frac{\ell + 1}{n+1} \chi\mu_n}{\mu_\ell} \right) \left( \zeta^2 + (1 - \zeta)^2 a + 2\zeta(1 - \zeta)\sqrt{a} \right).$$  \hspace{1cm} (5)$$

Here $\chi$ is the mass fraction of halogen, $\zeta$ is the relative fraction of halogen atoms in molecule, $a$ is the ratio of the pair potential constants,

$$\chi = \frac{x\mu_\ell}{x\mu_\ell + (1 - x)\mu_n}, \quad \zeta = \frac{(1 - \chi)\mu_\ell + \frac{\ell + 1}{n+1} \chi\mu_n}{(1 - \chi)\mu_\ell + \frac{\ell + 1}{n+1} \chi\mu_n}, \quad a \sim \frac{J_2 \alpha_2}{J_1 \alpha_1^2},$$

where $x$ is the n-alkyl molar fraction; $J_1$, $J_2$ are the ionization potentials of the atomic centers of n-alkane and n-alkyl, respectively; $\alpha_1$, $\alpha_2$ are the polarizabilities of the atomic center of n-alkane and n-alkyl; $\mu_n$, $\mu_\ell$ are the molar masses of the components (n-alkane and n-alkyl, respectively).

The relation (5) obtained in the framework of the model of independent atomic centers (C–H and C–G bonds) includes the data on their individual characteristics (their potentials of ionization and polarizabilities).

The estimation of the energy of intermolecular forces using experimental data of the thermophysical properties was carried out according to the formula:

$$|E_p| = \frac{u^2\alpha_p T}{\gamma} - \frac{N R T}{N_0 M}. \hspace{1cm} (6)$$

In the ratio (6), $u$ is the speed of sound, $\alpha_p$ is the isobaric coefficient of thermal expansion, $\gamma$ is the ratio of heat capacities.
Table 2. Intermolecular energies of different substances.

|                  | n-Decane     | Bromo-Decane | Chloro-Decane | Iodo-Decane | n-Decane + Bromo-Decane* |
|------------------|--------------|--------------|---------------|-------------|--------------------------|
| Thermodynamic    | 0.718        | 0.276        | 0.490         | 0.170       | 0.401                    |
| Calculation      | 0.698        | 0.272        | 0.476         | 0.170       | 0.410                    |
| by the formula   | 2.7%         | 1.4%         | 2.9%          | 0.0%        | 2.0%                     |

|                  | n-Octane     | Bromo-Octane | Chloro-Octane | n-Octane + Bromo-Octane* |
|------------------|--------------|--------------|---------------|--------------------------|
| Thermodynamic    | 0.731        | 0.241        | 0.467         | 0.383                    |
| Calculation      | 0.739        | 0.242        | 0.462         | 0.380                    |
| by the formula   | 1.1%         | 0.2%         | 1.0%          | 0.7%                     |

* A mixture of a hydrocarbon with a halohydrocarbon in a molar concentration of 1 : 1.

A good agreement between the values of the dispersion constants $B$, calculated using the formula (5) and the data on thermal physical properties, indicates the realism of the adopted model (see figure 1). Comparison of the obtained energy values with the data calculated on density makes opportunity to confirm that the energy of intermolecular forces is indeed proportional to the square of the opportunity (see figure 1 and table 2):

$$|E_p| = B\rho^2.$$  

This indicates the dominant contribution to the interaction energy of the energy of dispersive attractive forces ($m = 6$).

For a more accurate description of the energy of intermolecular forces, it is necessary to take into account the contributions to the energy of other forces – the energy of repulsive forces and the energy of the far-range binding forces, which is provided by relation (4). Many researchers supposed the existence of the far-range binding forces. However, experimental and theoretical proof of existence of these forces presented quite recently [5]. The nature of these forces by the authors [5] explained by the non-covalent interaction of C–H…C–H bonds due to the asymmetric electron density distribution near the $\pi$-bonds, because of the charge transfer. The principal attention is paid by authors and to dispersion forces.

3. Conclusion

Our research leads to the conclusion that the energy of dispersion attraction forces dominates in liquid hydrocarbons and their binary mixtures, that is proportional to the substance’s density squared. The constants of dispersion forces depend on the individual properties of C–H and C–G bonds and can be calculated according to the formula (5) obtained on the basis of a model of independent atomic centers proposed by the authors.

For a more accurate description of the intermolecular energy, it is necessary to take into account the energy of repulsive forces and energy of far-range bonding forces.
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