

**ON THE QUESTION OF THE RELATIONSHIP BETWEEN
THE ROTATIONAL MOTION OF MOLECULES
AND THE ALTERNATION OF PROPERTIES
IN HOMOLOGICAL SERIES**

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Abstract

In the paper the emphasis is placed on attempt to describe the effect of alternation of melting points in homologous series using the example of melting points of alkanes of normal structure from the frame of reference of the concept of rotational motion of molecules in a liquid. In the existing literature, the presence of separate sequences for the melting points of even and odd homologues is usually explained by packing effects, in which, due to different symmetry, even and odd representatives crystallize with different densities of the crystal lattice. However, this behavior can also be explained by the difference in the entropies of the rotational motion of molecules in the liquid phase, which is observed due to the different positions of the axis of rotation for even and odd homologues. The theoretically predicted difference in the moments of inertia for molecules with an even and an odd number of carbon atoms in the chain was confirmed by calculating the moments of inertia of *n*-alkane molecules, for which the atomic coordinates were optimized using density functional theory calculations

Keywords

Even-odd effect, moment of inertia, rotational motion of molecules, entropy of rotational motion, melting point

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Introduction. The phenomenon of alternation of the absolute values of some physicochemical properties is widely known in homologous series of compounds of the form $X(\text{CH}_2)_n\text{Y}$, where X and Y are a hydrogen atom, a hydrocarbon radical, or some functional group. The most striking and well-known example is the melting points of substances [1], in which case homologues with an even and odd number n form their own sequences (Fig. 1).

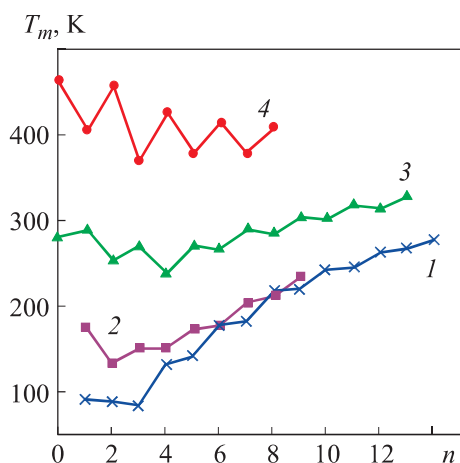


Fig. 1. Alternation of melting points in some homologous series $X(\text{CH}_2)_n\text{Y}$ (1 — X, Y = H; 2 — X = H, Y = Cl; 3 — X = H, Y = COOH; 4 — X, Y = COOH)

This phenomenon, also called the “even-odd effect”, was first demonstrated by Bayer [2] in the melting points of dicarboxylic acids. As a rule, at present it is customary to explain the even-odd effect on melting of homologues by packing effects [3–7]. It is usually assumed that, due to the different symmetry of the molecules of even and odd homologues, some of them have a more efficient crystal packing, as a result of which the molecular crystals of even or odd homologues have a higher density and, accordingly, a higher melting point. For homologues with a sufficiently large number of carbon atoms in the main chain (above six), Bond has come to the conclusion that this explanation to be quite acceptable [4].

However, it is necessary to take into account that at present, the manifestation of an even-odd effect has been recorded for a sufficiently large number of properties, and both related to the crystalline state of a substance and not. For example, an even-odd effect was found for such properties as spectral characteristics, reaction rate constants, biological properties and solubility, dipole moments, magnetic susceptibility, etc. [8–25].

Thus, at the moment it becomes clear that the even-odd effect is not a separate special case, but is rather widespread in nature. As a rule, the considered alternations of properties always show a single picture: the greatest difference in values is observed at the beginning of the homologous series, and then gradually fades away (see Fig. 1). In this case, the first members of the homologous series most often drop out of the general sequence.

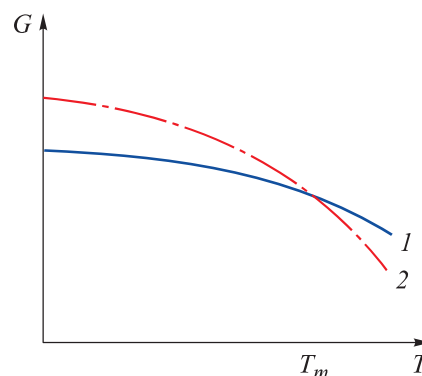
Discussion of the difference between even and odd homologues. In this paper, we attempted to look at the effect of alternation of melting points in homologous series using the example of melting temperatures of normal alkanes from the point of view of the concept of rotational motion of molecules in a liquid. The optimal structure for the solid phase is the one with the minimum total energy. In this case, for temperatures other than absolute zero, it is necessary to take into account the entropy effects. The most stable state of matter will be such that the Gibbs free energy is minimal [26]:

$$G = U + pV - TS. \quad (1)$$

With a change in temperature, the difference in the entropies of the phases leads to the fact that one of the phases begins to have a lower free energy and becomes more stable at this temperature, which causes phase transitions between allotropic modifications, as well as melting and crystallization.

Thus, melting can be represented as a competition between two phases, which is schematically shown in Fig. 2. At low temperatures, the solid phase

Fig. 2. Energy change of solid and liquid phases with increasing temperature (1 — solid phase; 2 — liquid phase)



has a lower Gibbs free energy, but at high temperatures the liquid phase has a lower Gibbs free energy due to the entropy term TS in Eq. (1). The phase transition occurs at the point corresponding to the equality of the Gibbs free energies of the two phases, which corresponds to the melting or crystallization temperature of the substance.

For the homologous series of normal alkanes (see Fig. 1), homologues with an odd number of carbon atoms have slightly lower melting points than even ones [27].

The diagram shown in Fig. 2 suggests that from the point of view of the change in the Gibbs free energy, the fundamental difference between even and odd homologues, based on Eq. (1), should be that even or odd homologues should have slightly different values of the entropy S relative to the general trend, while maintaining the constancy of the difference in the even and odd series, due to which the free energy of the liquid phase decreases with increasing temperature at a different rate and the properties of even and odd homologues form their own sequences.

The entropy term in Eq. (1) consists of several components [28]. Since, with a high degree of approximation, we can say that the total energy of a molecule can be represented in the form of mutually independent components

$$\varepsilon_i - \varepsilon_0 = \varepsilon_{\text{trans}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}} + \varepsilon_e,$$

then we can divide the molecular partition function into factors

$$Z = \sum_{i,j,k,l} g_{i,j,k,l} \exp\left(-\frac{\varepsilon_{\text{trans}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}} + \varepsilon_e}{kT}\right) = Z_{\text{trans}} Z_{\text{rot}} Z_{\text{vib}} Z_e, \quad (2)$$

where $g_{i,j,k,l} = g_{\text{trans}}^i g_{\text{rot}}^j g_{\text{vib}}^k g_e^l$ by virtue of the assumption of the independence of certain types of motion from each other. For this approximation, the grand partition function a mole of indistinguishable particles is determined by the equation

$$Q = \frac{(Z_{\text{trans}} Z_{\text{rot}} Z_{\text{vib}} Z_e)^{N_A}}{N_A!} = Q_{\text{trans}} Q_{\text{rot}} Q_{\text{vib}} Q_e,$$

$$Q_{\text{trans}} Q_{\text{rot}} Q_{\text{vib}} Q_e = \frac{Z_{\text{trans}}^{N_A}}{N_A!} Z_{\text{rot}}^{N_A} Z_{\text{vib}}^{N_A} Z_e^{N_A}.$$

Since thermodynamic quantities are evaluated in terms of $\ln Q$, and $\ln Q$ is equal to the sum of the logarithms of the partition function of all types of molecular motion, it is possible to calculate the individual contributions of each motion to thermodynamic functions, *incl.* into entropy:

$$S_{(T)}^0 = S_{\text{trans}}^0 + S_{\text{rot}} + S_{\text{vib}} + S_e. \quad (3)$$

Which of the entropy terms of Eq. (3) can be the reason for the difference in the properties of even and odd properties of homologues? Let us consider the calculation of each of them for three-dimensional ideal gas molecules. The corresponding values of entropy can be calculated using the components of the molecular partition function from Eq. (2):

$$S_{\text{trans}} = k \ln Q_{\text{trans}} + kT \left(\frac{\partial \ln Q_{\text{trans}}}{\partial T} \right)_P = R \ln \frac{Z_{\text{trans}}}{N_A} + RT \left(\frac{\partial \ln Z_{\text{trans}}}{\partial T} \right)_P; \quad (4)$$

$$S_{\text{rot}} = k \ln Q_{\text{rot}} + kT \frac{d \ln Q_{\text{rot}}}{dT} = R \ln Z_{\text{rot}} + RT \frac{d \ln Z_{\text{rot}}}{dT}; \quad (5)$$

$$S_{\text{vib}} = k \ln Q_{\text{vib}} + kT \frac{d \ln Q_{\text{vib}}}{dT} = R \ln Z_{\text{vib}} + RT \frac{d \ln Z_{\text{vib}}}{dT};$$

$$S_e = k \ln Q_e + kT \frac{d \ln Q_e}{dT} = R \ln Z_e + RT \frac{d \ln Z_e}{dT}.$$

The total partition function of the translational motion is calculated as [31]

$$\begin{aligned} Z_{\text{trans}} &= \int_0^{\infty} e^{-\alpha i_x^2} di_x \int_0^{\infty} e^{-\alpha i_y^2} di_y \int_0^{\infty} e^{-\alpha i_z^2} di_z = \\ &= Z_{\text{trans}, x} Z_{\text{trans}, y} Z_{\text{trans}, z} \frac{V (2\pi mkT)^{3/2}}{h^3}. \end{aligned} \quad (6)$$

Here V is the volume available for the translational motion of the molecule. As follows from Eq. (6), none of the factors is able to “distinguish” between even and odd molecules. The corresponding value of S_{trans} from Eq. (4) will similarly exhibit a single dependence for both even and odd members of the homologous series.

When calculating the vibrational partition function of a polyatomic molecule, it can be represented as a set of harmonic oscillators, each of which vibrates independently of the others. The number of such oscillators is equal to the number of degrees of freedom f of the molecule per vibrational motion. Then the vibrational partition function of a polyatomic molecule will be

$$Z_{\text{vib}} = \prod_{i=1}^{i=f} Z_{i,\text{vib}} = \prod_{i=1}^{i=f} \frac{1}{1 - \exp(-hv_i / (kT))},$$

where v_i is the main oscillation frequency of the i -th oscillator. The value of the vibrational partition function also turns out to be insensitive to the evenness and oddness of homologues.

The electronic partition function also does not distinguish between odd and even molecules. At temperatures $T < 10^3$ K, for most atoms and molecules, only the ground unexcited electronic level appears to be populated. Therefore, at room temperature $Z_e = g_0$, where g_0 is the statistical weight of the ground electronic level of a molecule or atom.

The most interesting is the consideration of rotational motion. It was shown that the entropy of rotational motion of molecules in the gas phase correlates with some physical properties of the liquid phase, in particular, the volumetric coefficient of thermal expansion [29]. At the same time, attempts to predict the melting points of alkanes on the basis of empirical or thermodynamic models were made earlier [30, 31]. We can draw conclusions that the contribution responsible for the difference between the even and odd homologues from these terms is the entropy of rotational motion, since only it is able to respond to the

different symmetries of even and odd homologues. Let us first consider the calculation of the rotational entropy for a molecule in the gas phase. In this case, the rotational entropy can be calculated from the partition function of the rotational motion (Eq. (5)).

The rotational partition function of a polyatomic nonlinear molecule is a function of the moment of inertia of the molecule, temperature, and also the symmetry of the molecule:

$$Z_{\text{rot}} = \frac{\sqrt{\pi}}{\sigma} \sqrt{\frac{8\pi^2 I_x kT}{h^2} \frac{8\pi^2 I_y kT}{h^2} \frac{8\pi^2 I_z kT}{h^2}}, \quad (7)$$

where I_x , I_y , and I_z represent the moments of inertia of the molecule about the three main axes of rotation. Since

$$RT \frac{d \ln Z_{\text{rot}}}{dT} = \frac{3}{2} \frac{RT}{T} = \frac{3}{2} R,$$

then Eq. (5) for calculating S_{rot} will have the form

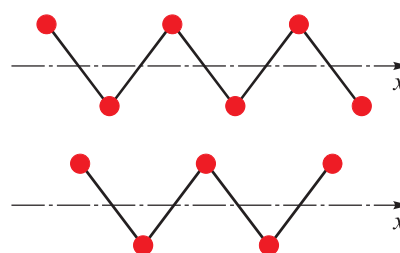
$$S_{\text{rot}} = R \left(\ln Z_{\text{rot}} + \frac{3}{2} \right) = \frac{1}{2} R \ln (I_x I_y I_z) + \frac{3}{2} R \ln T - R \ln \sigma + R \left(\frac{3}{2} + \ln \frac{\sqrt{\pi} (8\pi^2 k)^{3/2}}{h^3} \right). \quad (8)$$

Equation (8) is strictly valid for molecules in the gas phase. In the liquid phase, unlike gas, the molecules are in constant contact with each other, therefore, due to intermolecular interactions, the real entropy of the rotational motion of the molecules should be lower than that calculated by formula (8). The moment of inertia of molecules about a certain axis, used in Eqs. (7) and (8), can be calculated as the sum of the products of the masses of atoms by the square of their distance to the chosen axis:

$$I = \sum_i m_i r_i^2. \quad (9)$$

As the x axis, we take the main axis of rotation corresponding to the minimum possible moment of inertia of the molecule I_x . Obviously, in the case of a linear chain, for example, n -alkanes, the x axis will run along the main carbon chain. In this case, even and odd homologues in this case have a fundamental difference, which consists in the fact that they have a different character of the position of this axis (Fig. 3).

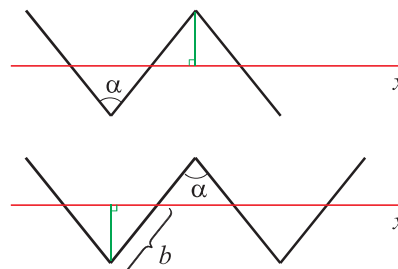
Fig. 3. The location of the axis of rotation with the minimum value of the moment of inertia for even and odd carbon chains



The aim of this research is to find a qualitative correlation between the melting temperatures of *n*-alkanes and the calculated moments of inertia about the main axis of rotation.

Results and discussion. Even homologues have a symmetric distribution of the heaviest carbon atoms about the *x* axis, while odd ones are asymmetric, which is why the rotation axis along this direction of the molecule is shifted towards the side with a large number of carbon atoms. Since formula (9) contains the square of the distance to the axis of rotation, this leads to the fact that for odd homologues a proper sequence of moments of inertia should be observed along this axis, which should be located slightly higher than for even ones. Let us show why this is so. Let us consider for simplicity the even and odd chain of carbon atoms and derive equation for them for calculating the moment of inertia about the *x* axis (Fig. 4).

Fig. 4. Geometrical parameters of carbon chains of even and odd homologues



Let us introduce the following notation: α is the tetrahedral angle, l is the length of the carbon-carbon bond, m is the mass of a carbon atom, b is the distance from a carbon atom to the axis of rotation along the bond line from the side of an even number of carbon atoms in the case of odd hydrocarbons, n is the number of carbon atoms in the chain.

For even chains, the axis of rotation will pass through the middle of the carbon-carbon bond, so it is obvious that

$$I_{\text{even}} = nm \left(\frac{1}{2} l \cos \frac{\alpha}{2} \right)^2.$$

For odd chains, the axis of rotation is shifted to the side with a large number of carbon atoms so that the total value of the moment of inertia is minimal. Let us derive an equation for calculating the moment of inertia:

$$I_{\text{odd}} = \frac{n-1}{2} m \left(\cos \frac{\alpha}{2} \right)^2 b^2 + \frac{n+1}{2} m \left(\cos \frac{\alpha}{2} \right)^2 (l-b)^2. \quad (10)$$

The value of b is found from the condition that the derivative of the moment of inertia with respect to b is equal to zero

$$\frac{dI_{\text{odd}}}{db} = (n-1) m \left(\cos \frac{\alpha}{2} \right)^2 b + (n+1) m \left(\cos \frac{\alpha}{2} \right)^2 b - (n+1) ml \left(\cos \frac{\alpha}{2} \right)^2 = 0;$$

$$\frac{dI_{\text{odd}}}{db} = 2nm \left(\cos \frac{\alpha}{2} \right)^2 b - (n+1) ml \left(\cos \frac{\alpha}{2} \right)^2 = 0,$$

from where

$$b = \frac{n+1}{2n} l. \quad (11)$$

Then, substituting the value of b from (11) into (10), we obtain

$$I_{\text{odd}} = \frac{n-1}{2} m \left(\cos \frac{\alpha}{2} \right)^2 \left(\frac{(n+1)l}{2n} \right)^2 + \frac{n+1}{2} m \left(\cos \frac{\alpha}{2} \right)^2 \left(l - \frac{(n+1)l}{2n} \right)^2.$$

Having built the graphs of the dependence $I = f(n)$ according to the derived relations for even and odd chains, we observe an even-odd effect decreasing with increasing chain length (Fig. 5).

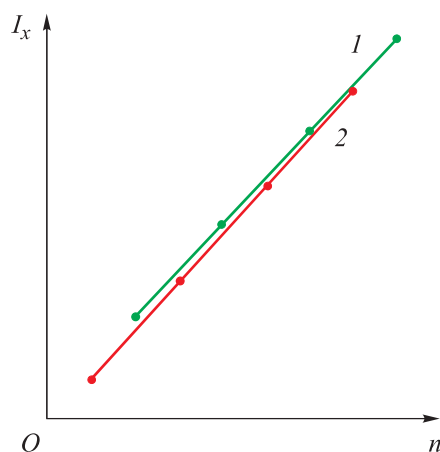


Fig. 5. Even-odd effect for theoretically calculated moments of inertia I_x of carbon chains (1 — even; 2 — odd)

Let us ask ourselves how the rotational motion of a molecule changes when it is transferred from the gas phase to the liquid phase. We assumed that, in addition to the appearance of the indicated intermolecular interactions, which prevent the free rotation of molecules, as a result of close contact of molecules with each other, conditions are created, as a result of which the rotation of molecules along certain axes becomes more preferable. The results of work [4], in which X-ray diffraction analysis of homologues of carboxylic acids of normal structure, located at a temperature close to the melting point, was carried out indicate that, at least near the melting point, homologues

with sufficiently long carbon chains are located in a single inhibited linear conformation. Thus, each molecule of such substances can be represented as being in a cell formed by neighboring hydrocarbon molecules (Fig. 6).

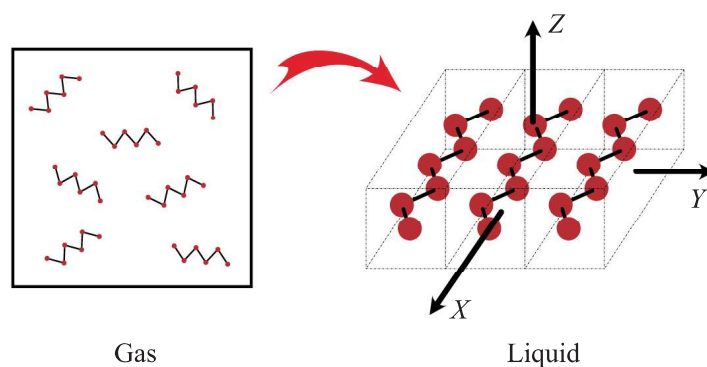


Fig. 6. Schematic representation of alkanes in the liquid phase and the cells they occupy

Since alkanes have an elongated molecular structure, presumably in a liquid the most preferable is the rotation of such molecules along the x axis, relative to which the molecule has the least resistance of neighboring molecules and the smallest moment of inertia I_x . Rotational oscillations along the y and z axes are limited by neighboring molecules and the conformational flexibility of the chains, as a result of which rotation of the molecule as a whole is impeded. Most likely, complete rotation does not occur at all [32], but rotational rocking of the molecule occurs relative to the equilibrium position. From formula (8) it is clear that the entropy of rotational motion is directly proportional to the value of the moment of inertia. If, under conditions of close contact of molecules in a liquid, the most probable is rotation (or rotational rocking) about the axis with the smallest moment of inertia, then lower melting temperatures correspond to a larger value of the moment of inertia I_x for odd homologous.

To determine the alternations of the moments of inertia and entropy of the rotational motion of real molecules relative to the x axis, a homologous series of alkanes of normal structure from methane to octane was used. The choice of such model compounds is due to the absence of strong intermolecular (hydrogen bond, Keesom forces, etc.) interactions in the homologous series of alkanes.

At the first stage, optimization of the geometry of molecules was carried out by density functional theory calculation using the PBE method using the 6-311++G(2d,2p) basis set. The calculations were carried out using the GAMESS software package (2019.R1) [33].

At the second stage, the obtained optimized coordinates were used to calculate the moments of inertia in our specially written program “Moments of inertia” [34]. The correctness of the obtained results was verified (for those compounds for which it was possible) by comparison with the database of computational chemistry and comparative tests of the *National Institute of Standards and Technology* (NIST) [35]. This comparison showed that similar results are obtained using other methods and basis sets.

In the course of the calculations, the following values of the moments of inertia were obtained [36], presented in Table.

Calculated values of the moments of inertia of the rotational motion of molecules in the gas phase for the homologous series of *n*-alkanes

Compound	Moments of inertia, Da · Å ²			Moments of inertia, kg · m ²			<i>T_m</i> , K
	<i>I_x</i>	<i>I_y</i>	<i>I_z</i>	<i>I_x</i> · 10 ⁻⁴⁶	<i>I_y</i> · 10 ⁻⁴⁴	<i>I_z</i> · 10 ⁻⁴⁴	
Methane	3.16			0.524	0.00524	0.00524	90.69
Ethane	6.19	25.19	25.19	1.03	0.0418	0.0418	90.30
Propane	17.00	59.93	67.67	2.82	0.0995	0.112	85.46
Butane	21.35	139.39	148.43	3.55	0.231	0.246	134.86
Pentane	29.39	260.87	274.89	4.88	0.433	0.456	143.40
Hexane	34.30	445.71	641.59	5.70	0.74	0.766	177.80
Heptane	41.54	697.46	717.52	6.90	1.16	1.19	182.50
Octane	46.71	1034.09	1056.27	7.76	1.72	1.75	216.30

It turned out that the theoretically predicted alternation of the moments of inertia along the *x* axis is indeed observed and has a character similar to the typical case of oscillations of properties in homologous series (Fig. 7).

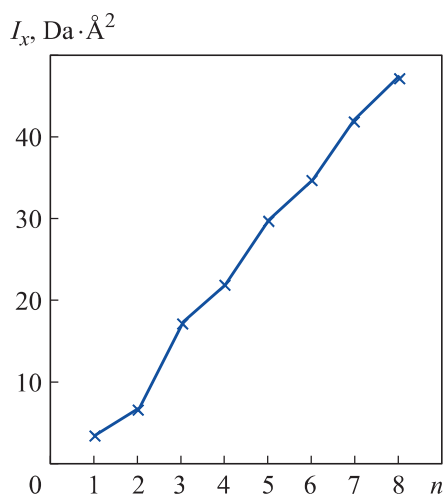


Fig. 7. Calculated alternation of the moments of inertia I_x for the homologous series of *n*-alkanes

For the moments of inertia I_y and I_z , orthogonal to the *x* axis, the calculated moments of inertia rise very quickly due to the square of the distance to these axes (Fig. 8). However, apparently, these values do not play a role in describing the rotational motion of molecules in the

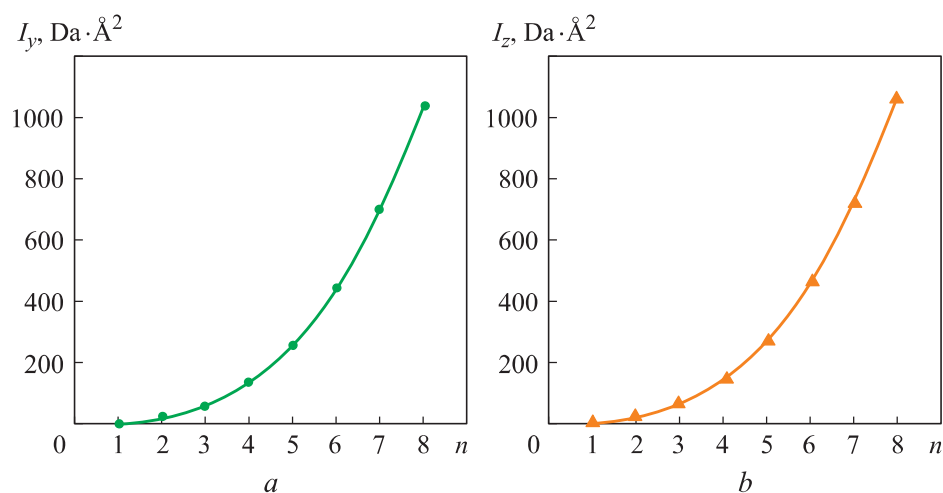


Fig. 8. Calculated moments of inertia I_y (a) and I_z (b) for the homologous series of n -alkanes

liquid phase due to the fact that the rotation of molecules as a whole object along these axes is not realized, and also due to the conformational mobility of the carbon chain.

It should be noted that the nature of the alternation of the moments of inertia of the rotational motion of n -alkanes fully corresponds to the observed pattern of changes in the melting temperatures, when lower melting points correspond to a larger value of the moments of inertia. However, it was possible to show only a qualitative dependence of the melting point on rotational motion, since the magnitude of the decrease in the entropy of rotational motion during the transfer of molecules from the gas phase to the liquid is unknown. In addition, since the moment of inertia of a molecule, strictly speaking, is a dynamic quantity due to conformational transitions and the presence of intermolecular interactions in a liquid, it is necessary to understand that in the case of more complex molecules, a different kind of an even-odd effect can also be observed. When considering such molecules, the following factors must be taken into account:

- the presence of short-range order in a liquid, due to the presence of functional groups and also depending on the general shape and symmetry of molecules;

- the presence of sufficiently strong intermolecular interactions (hydrogen bond, Keesom forces, Debye forces), leading to the formation of associates, which, during rotational rocking, behave differently from the original molecules, since they have a different arrangement of the rotation axes. For example, when dimers of carboxylic acids are formed, the resulting complex has other characteristics of symmetry and can rotate as a whole object.

Conclusion. The damped alternation of many properties in homologous series (as the temperature of melting) can be interpreted on the basis of the concept of rotational motion in a liquid.

There is a qualitative correlation between the melting temperatures of *n*-alkanes and the calculated moments of inertia relative to the main axis of rotation.

Homologous molecules with a sufficiently long carbon chain in a liquid, due to the presence of closely spaced neighboring molecules and conformational mobility, experience difficulties with rotation about axes located not along the main carbon chain. Because of this, rotational oscillations about the axis with the smallest moment of inertia I_x become the determining rotation for such elongated molecules in a liquid. With respect to this axis, homologues with an even and an odd number of carbon atoms in the chain have different symmetry and exhibit alternation of the moments of inertia, which leads to alternation of the entropy of rotational motion S_{rot} and, consequently, alternation of the melting points.

It is likely that later it will be possible to explain other properties that alternate in homological series.

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