

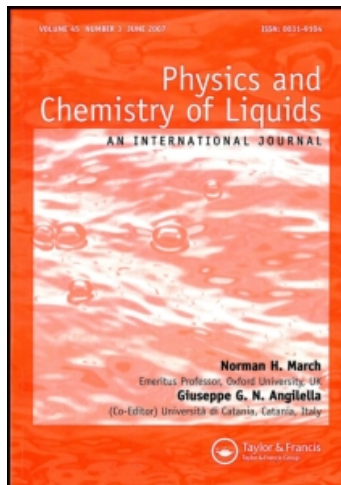
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X-RAY SCATTERING IN LIQUID PENTANE

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X-ray diffraction investigation of liquid *n*-pentane $\text{CH}_3 - (\text{CH}_2)_3 - \text{CH}_3$ was performed at 293 K. An angular distribution of X-ray scattered intensity was measured by applying $\text{MoK}\alpha$ ($\lambda = 0.71069 \text{ \AA}$) radiation. The electron density radial distribution function was numerically found using Fourier analysis. The mean distances between the neighbouring atoms were found. A simple model of short-range arrangement of the molecules was proposed.

Keywords: X-ray diffraction; Intra- and intermolecular interactions

1. INTRODUCTION

Pentane $\text{CH}_3 - (\text{CH}_2)_3 - \text{CH}_3$ (melting point -129°C , boiling point -36°C) has been studied in the gas [1], liquid [2] and crystalline phase [3]. The *n*-pentane crystal structure (at 123–133 K) is orthorhombic, space group Pbcn, and the molecule has a crystallographic twofold symmetry axis [4]. In the *n*-pentane molecule there are only σ -type covalent bonds between the carbon atoms /C(1)—C(2) bond length is $1.53 \pm 0.01 \text{ \AA}$ / and between carbon and hydrogen atoms /C(1)—H(11) bond length is $1.12 \pm 0.01 \text{ \AA}$ /. Owing to sp^3 hybridisation of carbon atoms, the angles between the bond directions are of about $109.5^\circ \pm 2^\circ$ [5]. Pentane has a zero dipole moment ($\mu = 0$) [6].

Molecules of *n*-alkanes have a great number of rotational states which correspond to local minima of potential energy and the energy

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TABLE I Physical (macroscopic density d , molecular mass M , and mean electron density ρ_0) and structural (mean effective number of electrons per hydrogen atom \bar{K}_H and per carbon atom \bar{K}_C) parameters of liquid n -pentane ($\sum_m Z_m$ denotes the sum of the atom numbers in one molecule)

d [g/cm ³]	M [g/mol]	ρ_0 [e/Å ³]	\bar{K}_H	\bar{K}_C	$\sum_m \bar{K}_m$	$\sum_m Z_m$
0.6262	72.15	0.2195	0.642	6.858	42.003	42

differences between conformations are not significant [7]. Results of electron diffraction studies in the gaseous n -pentane imply that at room temperatures the most probable are the following two conformations: synclinal-antiperiplanar (GT) and doubly anti-periplanar (TT). Their percent contribution is about 50% and 40%, respectively [1]. According to the spectroscopic studies [3], in a solid state n -pentane occurs in a doubly anti-periplanar [8] conformation. Since the absolute minimum of n -alkanes energy always corresponds to the T conformation of neighbouring chains [7], the considerations presented in this paper concern the doubly anti-periplanar conformation of n -pentane molecule.

This paper reports results of X-ray structural studies of liquid n -pentane. The aim of the study is the analysis of the radial distribution function (RDF) determined from the diffraction pattern obtained for liquid n -pentane at 293 K. The model of the most probable short-range ordering of n -pentane molecules in the liquid phase is also proposed.

Physical and structural parameters of the liquid studied are given in Table I. The n -pentane sample studied was purchased from Aldrich-Chemie, Germany.

2. EXPERIMENTAL

Structural studies were conducted using an X-ray diffractometer equipped with a horizontal counter goniometer HZG3. The source of MoK $_{\alpha}$ radiation was a sealed tube working at the optimum voltage $U = 40$ kV and intensity $I = 35$ mA. The radiation was monochromatized by reflection from the (002) planes of graphite [9].

Measurements were performed for the angles in the range $3^\circ \leq \vartheta \leq 60^\circ$ at every $(0.2 \pm 0.01)^\circ$, where 2ϑ is the angle of

scattering, by the transmission method [10] with the incident and deflected beams symmetrical with respect to the surface of the sample. Small-angle scattering ($0^\circ < \vartheta < 3^\circ$) results were extrapolated to the origin of the coordinate system using a second-order function [11]. Intensity of the scattered radiation was measured by a proportional counter VA-G-120, coupled with the calculating unit, and the results were fed to a computer. Deviations in intensity due to the instability of the diffractometer work were of about 1% in the whole range considered.

The studies were carried out in a special cuvette with exchangeable plates, constructed in our laboratory [12]. The sample consisted of a layer of pure *n*-pentane 1 mm thick, placed between two windows of 0.025 mm foil. The material used and the thickness of the windows permitted us to neglect the absorption by the windows, which has been experimentally verified prior to measurements.

The cuvette was connected with a flow-through ultrathermostat U-10. Measurements were carried out at $(20.0 \pm 0.1)^\circ\text{C}$ controlled by a copper-constantan thermocouple and a sensitive mirror galvanometer GL-1. Inside the cuvette, the temperature was measured by a temperature probe made by Testoterm GmbH&Co Lenzkirch, Germany. Measurements were performed for different times of counting and a few times repeated so that a final result was an average.

3. CALCULATIONS

The radial distribution function of electron density $\rho(r)$ for liquid *n*-pentane was determined from the modified Warren-Krutter-Morningstar equation [13] in the form

$$\sum_m \bar{K}_m 4\pi r^2 \rho(r) = \sum_m \bar{K}_m 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^\infty \text{Si}(S) \sin(Sr) ds, \quad (1)$$

where $K_m = (f_m/f_e)$ is the effective number of diffracting electrons in the atom m , and

$$f_e = \sum_m f_m / \sum_m Z_m \quad (2)$$

is the mean value of the atomic factor for a molecule per a single electron, f_m is the atomic factor of the m -th atom and Z_m is the number of electrons in the atom, see Table I.

The mean effective number of scattering electrons was found from the integral average

$$\bar{K}_m = \frac{1}{S_2 - S_1} \int_{S_1}^{S_2} K_m dS, \quad (3)$$

where S_1 and S_2 are the lower and upper bounds of the range of S values. The result of Fourier transform is affected by the errors arising due to the limited range of intensity measurements. In the computer program for calculation of radial functions from the angular ones [11] we use the value of S_{\max} matching the experimental conditions. In our experiment $S_1 = 0.43$ and $S_2 = 4\pi \sin \vartheta_{\max} / \lambda = 15.31 \text{ \AA}^{-1}$ for the MoK_{α} radiation. The value of $i(S)$ appearing in Eq.(1) is obtained from:

$$i(S) = \frac{\bar{I}(S)/N - \sum_m f_m^2}{g^2(S)} \quad (4)$$

This expression represents the structurally sensitive part of the total coherent intensity $\bar{I}(S)/N$ per a single molecule, $\sum_m f_m^2$ denotes the theoretical independent scattering on atoms of one structural unit.

According to Warren [14], $g(S) = f_e$, where f_e is defined by Eq. (2). In order to smooth the erroneous undulations of the functions of density distribution originating from improper truncation of the experimental functions $\bar{I}(S)$, a temperature dependent factor was introduced [11] $\exp(-\alpha^2 S_{\max}^2)$. The radial distribution functions were calculated for $\alpha = 0.05$. The mean electron density was found from the formula [15]:

$$\rho_0 = \frac{10^{-24} N_A d \sum_m Z_m}{M}, \quad (5)$$

where d is the macroscopic density of the liquid studied, N_A – the Avogadro number, M – molecular weight (see Tab. I). The integer in Eq. (1) was calculated numerically by the Simpson method for $0 \leq r \leq 20 \text{ \AA}$, with a step of $\Delta r = 0.05 \text{ \AA}$.

The corrections for background [16], polarisation [17] and absorption [18] were taken into account in finding the angular distribution

of the scattered radiation intensity. Experimental data were normalized according to the Krogh-Moe [19] and Norman [20] method. The ranges of uncertainty for the structural parameters determined are as follows: $1 \leq \bar{r} \leq 4 \text{ \AA}$, $\Delta\bar{r} = \pm 0.02 \text{ \AA}$, for $\bar{r} > 4 \text{ \AA}$: $\Delta\bar{r} = \pm 0.05 \text{ \AA}$ [21]. The maximum experimental error in determination of the radial distribution functions was estimated to be $\pm 3\%$ [22].

4. RESULTS

The normalized angular distribution function of $\bar{I}(S)$ (Fig. 1) was found to have the main maximum for $S = (1.36 \pm 0.01) \text{ \AA}^{-1}$

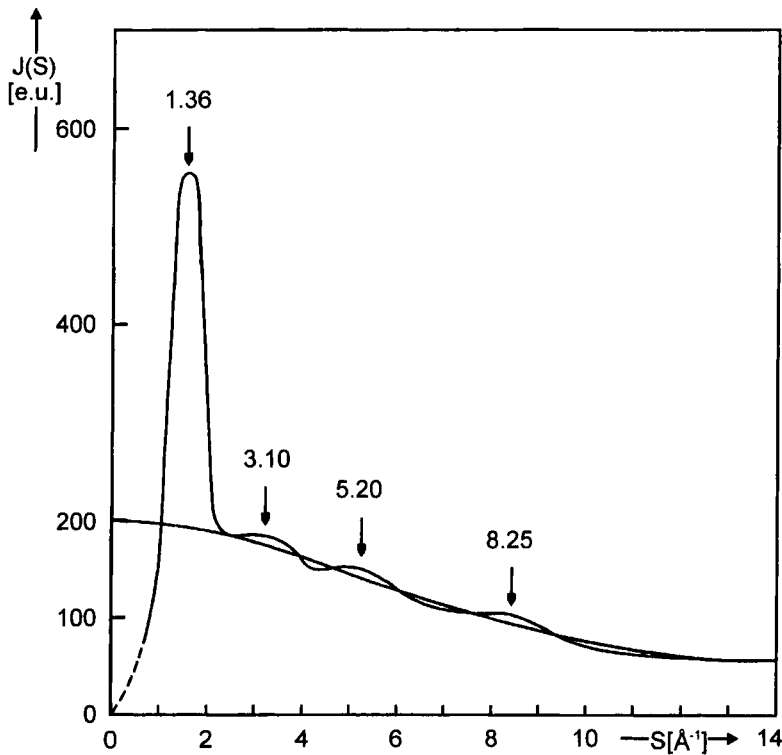


FIGURE 1 The normalized, experimental curve of angular distribution of X-ray scattered intensity in liquid *n*-pentane.

(where $S = 4\pi \sin \vartheta / \lambda$) which corresponds to the mean intermolecular distance in liquid *n*-pentane of $\bar{d} = 4.63 \text{ \AA}$ determined directly from Bragg equation [23].

The most probable intermolecular distances were found from the positions of the maxima of the RDF (Fig. 2).

The first two maxima were ascribed to the interferences within the *n*-pentane molecule (Fig. 3). However, no physical meaning was ascribed to the partial maximum at $\bar{r} = 0.80 \text{ \AA}$. In the range of the argument below 1 \AA , the values of RDF making the interpretation difficult or even impossible (for example the negative ones) are not uncommon. They seem to be due to some approximations assumed

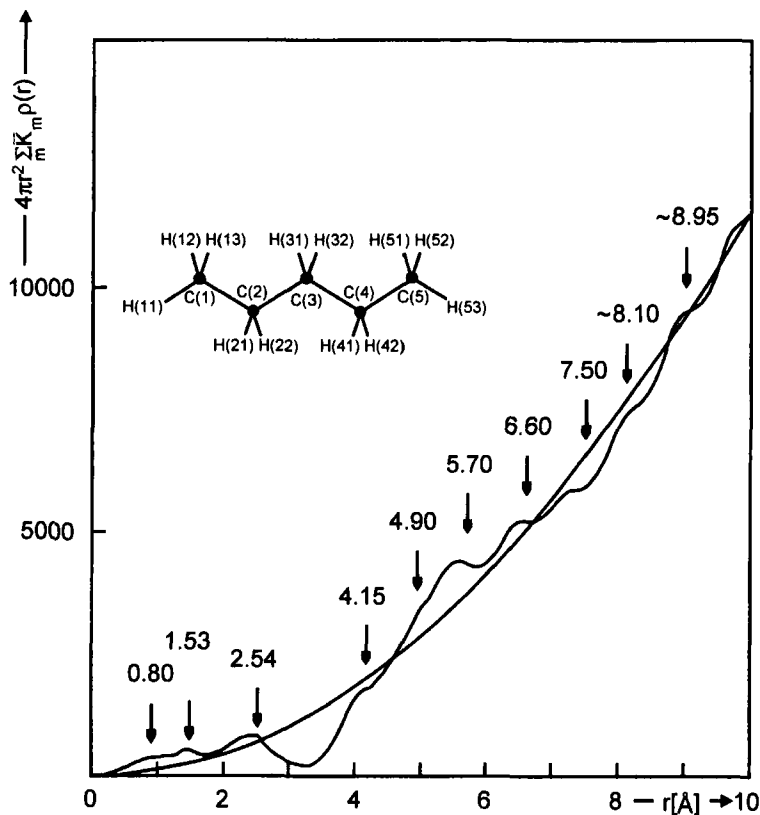


FIGURE 2 Electron density radial distribution function of liquid *n*-pentane.

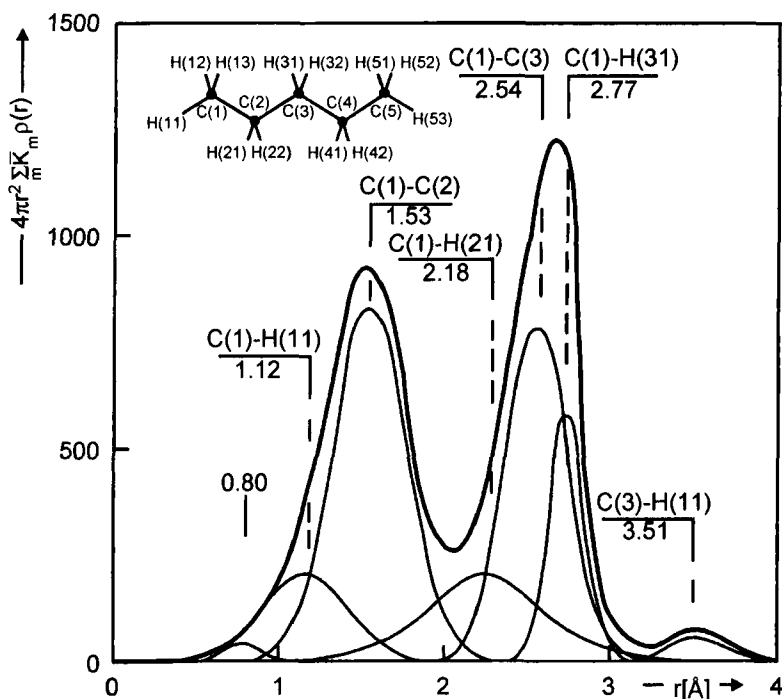


FIGURE 3 The theoretical RDF of *n*-pentane decomposed into its atomic peaks.

in the method, *e.g.*, to the extrapolation of small angle scattering results [11]. Figure 3 shows the calculated radial distribution curve of *n*-pentane decomposed into the various atomic peaks [24].

5. DISCUSSION

The most probable simple configurations of neighbouring molecules in the liquid in question can be examined by fitting the positions of the maxima of the RDF to the distances between the centres of neighbours, resulting from their van der Waals models. Such models can be constructed on the basis of the bond lengths within the molecule and of the van der Waals radii of C and H atoms. The size of an *n*-pentane molecule is 9.4 Å (length) × 3.8 Å (width) × 3.5 Å (height). On the average it takes a volume of $V = 191.3 \text{ \AA}^3$, whereas

an increment of the molecule volume [25] is $V^{\text{incr}} = 94.0 \text{ \AA}^3$. The packing coefficient of molecules in liquid *n*-pentane is $k = 0.49$.

Taking into regard the size of the *n*-pentane molecule, the first two maxima of the RDF function were ascribed to the interatomic distances inside this molecule, Table II.

The first maximum of RDF, for $\bar{r}_1 = 1.53 \text{ \AA}$ was ascribed to the interactions between the carbon and hydrogen atoms $\text{C}(1) - \text{H}(11) = 1.12 \text{ \AA}$, and between the neighbouring aliphatic carbon atoms in the chain $\text{C}(1) - \text{C}(2) = 1.53 \text{ \AA}$. By differentiation of the experimental RDF and the sum of particular partial maxima, the presence of another maximum at $r = 0.80 \text{ \AA}$ was revealed. However, no physical interpretation of this maximum was given.

The second maximum on the RDF function for $\bar{r}_2 = 2.54 \text{ \AA}$ was assigned to the three interatomic distances inside the *n*-pentane molecule: $\text{C}(1) - \text{H}(21) = 2.18 \text{ \AA}$, $\text{C}(1) - \text{C}(3) = 2.54 \text{ \AA}$ and $\text{C}(1) - \text{H}(31) = 2.77 \text{ \AA}$. As the first two maxima of RDF are not isolated, the areas under them could not be calculated separately. Instead, the area under the two of them was calculated by the Simpson method and the result was compared with the result of theoretical calculations, Table II.

From among the geometrically simplest mutual arrangements, the only one for which the distances between the mass centres are smaller than 6 \AA are those in which the chains of neighbouring molecules are parallel. The smallest distance between the centres of mutually perpendicular molecules (assuming the shape of the letter T) is 6.60 \AA . This distance corresponds exactly to the position of the 6th RDF maximum, Figure 2. The collinear arrangement in which the chains of neighbouring molecules are placed one after the other,

TABLE II Theoretical areas of the discrete maxima and corresponding intramolecular interactions

Maximum [Å]	Intramolecular distances [Å]	Theoretical areas $Q_T = 2 \cdot \bar{K}_C \cdot \bar{K}_H \cdot n[e^2]$
1.53	$\text{C}(1) - \text{H}(11) = 1.12$	$2 \cdot \bar{K}_C \cdot \bar{K}_H \cdot 12 = 105.7$
	$\text{C}(1) - \text{C}(2) = 1.53$	$2 \cdot \bar{K}_C \cdot \bar{K}_C \cdot 4 = 376.3$
2.30	$\text{C}(1) - \text{H}(21) = 2.18$	$2 \cdot \bar{K}_C \cdot \bar{K}_H \cdot 18 = 158.6$
	$\text{C}(1) - \text{C}(3) = 2.54$	$2 \cdot \bar{K}_C \cdot \bar{K}_C \cdot 3 = 282.2$
	$\text{C}(1) - \text{H}(31) = 2.77$	$2 \cdot \bar{K}_C \cdot \bar{K}_H \cdot 12 = 105.7$

leads to the distance between the molecule centres equal to 9.40 Å. As at such distances the local ordering progressively disappears, the collinear orientation can be disregarded. The arrangement intermediate between parallel and perpendicular seem to be less probable because they would lead to a too small packing.

The third maximum of RDF corresponds to the intermolecular distances from 3.75 Å to 4.60 Å with the most probable one of $\bar{r}_3 = 4.15$ Å. The fourth maximum is attributed to the distances from the range 4.60 to 5.20 Å with the mean distance of $\bar{r}_4 = 4.90$ Å. The fifth maximum is assigned to the distances from the range 5.20 Å to 6.25 Å, with the mean value of $\bar{r}_5 = 5.70$ Å.

As follows from the van der Waals model of the *n*-pentane molecule the RDF should have a maximum for $\bar{r} \approx 3.50$ Å if the molecules are closely packed one over the other and for $\bar{r} \approx 3.80$ Å if the molecules are arranged parallel to one another with the parallel molecules axes. The three RDF maxima \bar{r}_3 , \bar{r}_4 , \bar{r}_5 correspond to \bar{r} values higher than predicted for close molecular packing side by side or one over another. This fact can be explained assuming that the molecules are in mutually parallel arrangement but simultaneously shifted by about 2.50 Å along the chain axis [26].

There is a possibility of such intermolecular configurations in which the molecules are parallel, shifted with respect to one another and rotated by the right angle.

The 6th RDF maximum originates from molecules at a distance of 6.20 Å to 7.00 Å, and the most probable distance is $\bar{r}_6 = 6.60$ Å. It corresponds to the perpendicular arrangement (in the shape of the letter T) of neighbouring molecules.

These results are also consistent with the values presumed in the conformational structure investigation of *n*-pentane performed by empirical and semi-empirical MO-LCAO calculations [27]. The results have also been confirmed by the conformation analysis based on minimization of the potential energy [28].

The 7th maximum for $\bar{r}_7 = 7.50$ Å corresponds to the distance between the second neighbours in the side by side configuration of parallel molecules. Further maxima observed at 8.10 Å and 8.95 Å were not interpreted. They are strongly broadened which indicates progressing disappearance of local ordering.

6. CONCLUSIONS

The methods employed allowed a determination of the mean structural parameters (the inter- and intramolecular distances) and local ordering of molecules in liquid *n*-pentane. The appearance of distinct maxima in the angular distribution function of X-ray scattered radiation and radial distribution function of electron density obtained for liquid *n*-pentane indicates the presence of a short-range ordering in *n*-pentane up to a distance of about 8 Å.

The maxima in the range $1 \text{ \AA} < \bar{r} \leq 3 \text{ \AA}$ correspond to intramolecular interactions, whereas those appearing in the range from 4.15 Å to 7.50 Å are due to intermolecular diffraction.

The radial and angular distribution functions obtained allowed us to conclude that dominant is the parallel intermolecular configuration for $\bar{r} \approx 4.10 \text{ \AA}$ to 5.50 Å in which chains of the molecules are not only shifted relative to one another but also rotated by the right angle.

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