

# The Structural Characteristics and Viscosity of Liquids within a Hole Model

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**Abstract.** Experimental X-ray or electron-diffraction research of liquid allows to reliably assess the size of a lattice seat and holes in quasi-crystalline structures. According to the results of such research, lattice constants for a series of certain n-paraffins were calculated. The author used a hole model of liquids to obtain expressions which were later used to calculate enthalpies of activation of viscous current of n-alkanes and their mixtures. It allowed to connect the experimental work on definition of temperature dependency of liquids viscosity to the calculation of structure properties of liquid mixtures of non-electrolytes. Partly, such calculation was done while solving a problem of the composition of a surface layer of n-alkanes mixtures.

## 1. Introduction

The structure of a liquid, its molecular order and structural characteristics of liquid systems are determined by the atomic composition of molecules, their shape and intermolecular interaction. The only objective criterion which allows to reliably identify any of the structural parameters, e.g. specify the size of a lattice seat in the quasi-crystalline structure of a liquid, is experimental X-ray or electron-diffraction (neutron diffraction) research of liquid structures that have widely spread for the last 50 years.

## 2. Diffraction of Electrons of N-paraffins and Their Lattice Constants

In paper [1] using a method of electron diffraction the author researched the crystal structure of n-paraffins in general and n-alkanes in particular with the number of carbon atoms  $C_{18} \div C_{30}$  at crystallization temperature. The results obtained by A. Smith are represented in Figures 1-3 as a picture of electron diffraction on trikozane chain molecules (Fig.1) as well as models of packing of n-alkane segments and its molecules (Fig. 2,3) at different projections based on experimental calculations and findings. Approximate parameters and lattice constants for single solid n-paraffins are given in Table 1.

## 3. Viscosity and calculation of molecular parameters of n-alkanes and their mixtures

By solving the combined equations based on equations [2] specified for each of the n-alkanes considering approximated parameters and lattice constants (Table 1),

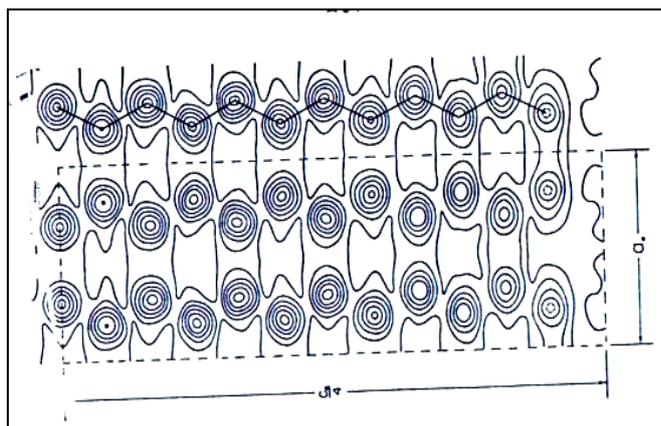
$$\begin{aligned} \nu(C_n)_{mol} &\equiv r_n \nu_0 = 2\nu(C_n)_{CH_3} + (n-2)\nu(C_n)_{CH_2} \\ r_n &= 2r(n)_{CH_3} + (n-2)r(n)_{CH_2} \end{aligned} \quad (1)$$



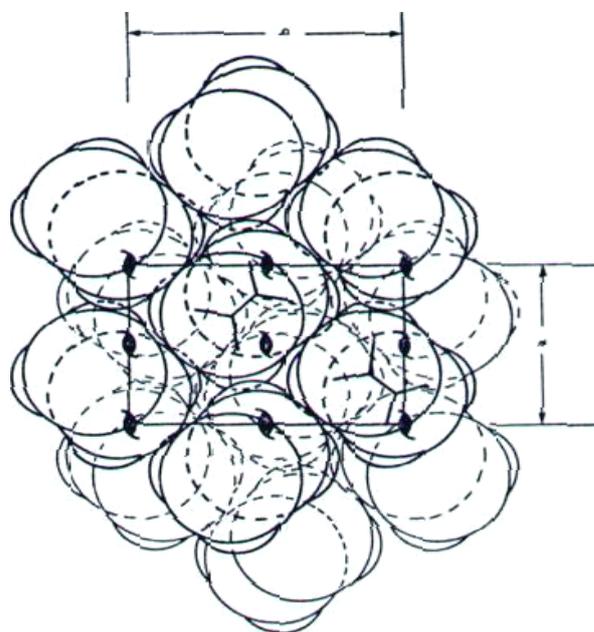
$$v(n)_{CH_3} = r(n)_{CH_3} \cdot v_0,$$

$$v(n)_{CH_2} = r(n)_{CH_2} \cdot v_0.$$

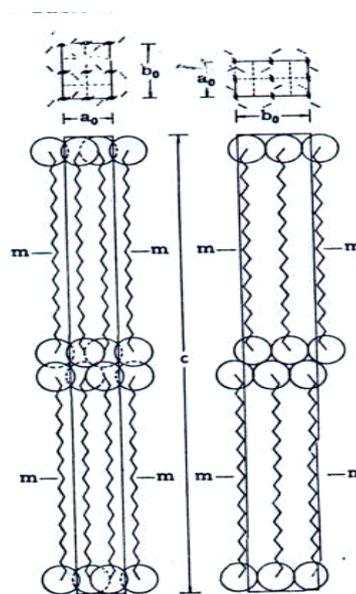
( $n = 21, 23, 25, 27, 29$ ;  $r$  – number of sections in an  $n$ -alkane chain), it became possible to calculate averaged values of  $\bar{v}_{CH_3}$  and  $\bar{v}_{CH_2}$  volumes as well as the size of a lattice seat (or hole),  $v_0$ , in the quasi-crystalline lattice with vacancies (holes).



**Figure 1.** A randomly-scaled Fourier projection in plane (010) for  $n$ -trikozane [1].



**Figure 2.**  $N$ -trikozane segments packing in  $ab$ -projection.



a) b)

**Figure 3.**  $N$ -trikozane segments packing in  $ac$  (a)- and  $bc$  (b)-projections.

**Table 1.** Approximate parameters and lattice constants for n-alkanes.

Alkanes	$a_0^*, \overset{o}{A}$ [1]	$b_0^*, \overset{o}{A}$ [1]	$c_0, \overset{o}{A}$ [1]	$\nu_{mol}^{exp} / r$ cm <sup>3</sup> /mol	$\nu_{CH_2},$ cm <sup>3</sup> /mol	$\bar{\nu}_{CH_2}$ cm <sup>3</sup> /mol	$\bar{\nu}_{CH_3}$ cm <sup>3</sup> /mol	$\nu_0$ cm <sup>3</sup> /mol
n-C <sub>21</sub> H <sub>44</sub>			57,30±0,08	15,286	13,974			
n-C <sub>23</sub> H <sub>48</sub>			62,31±0,10	15,160	13,697			
n-C <sub>25</sub> H <sub>52</sub>	4,970± 0,005	7,478± 0,005	67,41±0,10	15,088	13,960	13,977	26,810	14,212
n-C <sub>27</sub> H <sub>56</sub>			72,59±0,10	15,044	14,215			
n-C <sub>29</sub> H <sub>60</sub>			77,70±0,18	14,993	14,022			

\* Note. The parameters are equal within an experimental error for hydrocarbons.

The calculations are also shown in Table 1 and are further used as parameters for the whole series of polymerhomologs – n-alkanes. These lattice constants were necessary to research surface tension of n-alkane mixtures, and calculate composition and density profile of the surface layer in such systems [3].

To evaluate the  $r(n)$  parameter in formulas (1), we used  $r = r(H_{act})$  dependence, which, the lattice seat size volume  $\nu_0$  remaining, allows to calculate the number of seats in a lattice per molecule of pure r-mer,

$$r = \frac{\mu}{\rho \nu_0 (1 + \exp(-H_{act} / RT))}, \quad (2)$$

through the enthalpy of hole formation,  $H_{act}$ , for the given temperature, T.

In its turn, using equation (2) required to identify the criterion to calculate the amount of the hole formation energy,  $\Delta G_{hole}$ , and, therefore, consider the questions relating to the enthalpy of viscous flow activation.

Knowing the enthalpy of viscous flow activation allows to calculate some other structural liquid characteristics, such as the first coordination number,  $z_1$ , share of vacancies in homogeneous phase of a liquid system,  $\varphi_B$ , the first coordination sphere radius,  $\sigma_1$ , and the coefficient of particles packing in a lattice,  $k_{yn} \equiv \varphi_A$ , the latter relating to the method of molecules packing in a dense quasi-crystalline liquid system [2].

In paper [4], to obtain the necessary equations the authors use Frenkel's activation theory of viscous properties of a liquid. According to the theory, the viscosity of a liquid  $\eta$  is identified as

$$\eta = A(T) \cdot \exp H_{act} / kT, \quad (3)$$

where  $A(T)$  is a pre-exponential factor that is dependent on the temperature,  $H_{act}$  is enthalpy of activation of viscous current,  $k$  is Boltzmann constant, and  $T$  is an absolute temperature.

An immediate application of equation (3) for calculating dynamic viscosity coefficients of liquids within a wide temperature range is difficult due to absence of well-grounded dependence of activation enthalpy on the temperature and other structure and energy factors of liquid systems.

By studying this issue the researchers came to a conclusion that such a connection between this quantity and micro structural characteristics of a substance (first coordination number, pair interaction potential, effective molecule sizes) exists.

Therefore, the authors of paper [4] and the author of the current research used a hole model to obtain equations that can be used for practical calculation of enthalpy of activation of viscous current, which generally allows to relate experimental work that aims to determine a temperature dependence of liquids viscosity to calculations of structural characteristics of liquid systems [5,6].

According to Frenkel's theory [7], for isobaric thermal expansion coefficient,  $\alpha_p$ , and isothermal compression coefficient,  $\beta_T$ , the following occurs:

$$\alpha_p = \frac{V - V_0}{V_0} \cdot \frac{H_{act}}{kT^2},$$

$$\beta_m = \frac{V - V_0}{V_0} \cdot \frac{v_0}{kT}. \quad (4)$$

Consequently, it is possible to determine enthalpy of activation of viscous current as follows:

$$H_{act} = \frac{\alpha_p T}{\beta_m} \cdot v_0, \quad (5)$$

in which the energy of viscous current activation is considered to be equal to work against intermolecular forces in a liquid to create a hole with  $v_0$  capacity [4].

Such an approximation is quite possible for temperatures within substance melting boundaries when a change in system's entropy caused by formation of new holes is not big, and the work done to form holes can be considered to be almost equal to variation of Gibbs energy in a system. With even a slight excess of several kelvins over the melting temperature, it is recommendable that an entropic constituent be considered.

If n-alkanes are considered to be liquids whose properties make them close to ideal, entropic correction for a system's energy for mixture of chain molecules  $A$  and holes-monomers  $B$  can be identified according to the following Flory's equation for chain molecules:

$$\frac{\Delta S}{R} = \varphi_A \ln \varphi_A + \varphi_B \ln \varphi_B. \quad (6)$$

For chain molecule solutions in which there is interaction between segments of r-mers, thermodynamic functions of mixing should be calculated considering that interaction. In further research [8,9], the above-stated approach is used for the occurrence when not all the segments in molecules of sorts 1 and 2 are identical.

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