

A relation between X-ray diffraction based liquid structure and packing coefficient

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Abstract. A relation between the liquid structure and the molecules packing coefficient has been derived on the grounds of the experimental results of X-ray diffraction studies. The packing coefficient k was assumed to be a criterion of correctness of the structural models of 2-methyl-1-propanol and 2-methyl-2-propanol based on experimental results. This coefficient was estimated from the specific volumes of molecules V_0 , volumes of elementary pseudocells V and the number of molecules comprised into these pseudocells. The volumes V of pseudocells were estimated from the same X-ray diffraction pattern as was used for determination of the liquid structure. The determined values of the packing coefficient support the chain-like structure of associates of liquid 2-methyl-1-propanol and reject the chain-like structure for liquid 2-methyl-2-propanol.

Keywords. X-ray scattering pattern; molecules packing coefficient; structural model of the liquid.

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1. Introduction

Although no rigorous periodic internal structure exists in liquids, they still reveal some tendency towards ordering, namely, their molecules are statistically densely arranged and some intermolecular distances are distinguished. As a result of the statistical arrangement of molecules, a liquid subjected to X-ray investigation reveals a spherical symmetry. The diffraction patterns show more or less broadened rings. These patterns are the basic experimental data both for the formulation of the structural model of the liquid (Mikusińska-Planner 1979, 1983) and for estimation of the packing coefficient (Mikusińska-Planner 1986).

A structural model of a liquid is found from the analysis of radial functions of electron, atom or molecular density obtained by Fourier inversion of the experimental scattering data. However, as the X-ray patterns obtained for liquid are broadened, they are not as convenient for numerical analysis as the patterns obtained for crystals. Therefore structural information inferred from X-ray diffraction patterns for liquids is based on the model-theoretical interpretations. Assuming the most probable model of intermolecular interactions for which the calculated scattering pattern agrees best with the experimental one, we can estimate the number of molecules x per an elementary pseudocell. The volume of this cell, \bar{V} , is found from the radius of the so-called first coordination sphere \bar{R} , according to the spherical relation:

$$\bar{V} = 4\pi\bar{R}^3/3. \quad (1)$$

The notion of a spherical elementary pseudocell is justified by the spherically-symmetric distribution of molecules in the liquid, which is confirmed by the broadened rings in the diffraction pattern. The mean value of the radius \bar{R} is approximately determined from the position of the main maximum in X-ray scattering pattern

$$\bar{R} \approx 7.72/s(\max) - 0.3, \quad (2)$$

where $s(\max) = 4\pi \sin \theta(\max)/\lambda$, 2θ the angle of scattering and λ the X-ray scattering wavelength. The correcting factor 0.3 for molecular liquids has been found empirically (Voigtlaender-Tetzner 1958).

By analogy with the packing coefficient defined for crystals (Van Meerssche and Feneau-Dupont 1976) we can define the corresponding packing coefficient of molecules in liquids

$$k = V_0/(\bar{V}/x), \quad (3)$$

where V_0 is the specific volume of the molecule and \bar{V}/x is the volume available for one molecule in a pseudocell. The determined value k is correct only when it falls within the range $0.51 \leq k \leq 0.58$ as the values $k > 0.58$ correspond to the crystal phase and the values $k < 0.51$ to the gas phase (Kozhin 1968). The right coefficient value is, however, obtained only when the assumed model of intermolecular liquid structure in a given liquid is correct. If this model is not correct, the number of molecules, x , in one elementary pseudocell is wrongly estimated and the value of the k coefficient goes beyond the limit of values admissible for liquid phase.

2. Specific volume of molecules

The specific volume of a molecule may be found from its chemical structure, the length of bonds and van der Waals radii of atoms and functional groups. As an example we shall estimate it for a molecule of 2-methyl-1-propanol. Its shape and dimensions required are given in figure 1. The figure presents three orthogonal projections of $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$ molecule model onto three mutually orthogonal planes. The shape of the molecule can be approximated by a sphere and limited by three radii r_1, r_2, r_3 making the mean radius of

$$\bar{r} = (r_1 + r_2 + r_3)/3 = 3.03 \text{ \AA}, \quad (4)$$

where $r_1 = 3.00 \text{ \AA}$, $r_2 = r_3 = 3.05 \text{ \AA}$. The real radius of the molecule, r_0 , is however, significantly shorter than $\bar{r} = 3.03 \text{ \AA}$. The latter is henceforth called the maximum radius of the molecule $\bar{r} = r_{\max}$. The maximum radius r_{\max} determines the maximum volume of the molecule, $V_0 = 116.5 \text{ \AA}^3$. The areas of the model projections onto the three orthogonal planes (figure 1) were found to make only 76.85% of the area of sphere determined by the maximum radius $r_{\max} = 3.03 \text{ \AA}$. Thus, the spherical volume corresponding to the real molecule is

$$V_0 = (76.85 \times 116.5/100) \text{ \AA}^3 = 89.5 \text{ \AA}^3. \quad (5)$$

The real specific radius r_0 of a 2-methyl-1-propanol molecule is therefore 2.77 \AA .

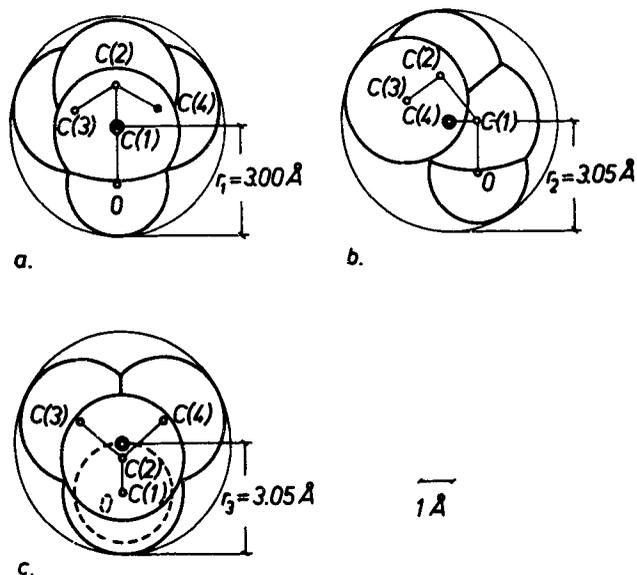


Figure 1. A model of 2-methyl-1-propanol molecule projected onto three orthogonal planes.

Table 1. Specific radii and volumes of molecules.

Alcohol	\bar{r}_0	\bar{V}_0
2-methyl-1-propanol	2.7 Å	82.4 Å ³
2-methyl-2-propanol	3.03 Å	116.5 Å ³

Taking into account the earlier results of specific radii of molecules reported by other authors (Vyrodov *et al* 1964) $r_{\text{theor}} = 2.69 \text{ \AA}$ and $r_{\text{vol}} = 2.64 \text{ \AA}$, the mean value of a 2-methyl-1-propanol molecule is estimated to be

$$\bar{r}_0 = (r_0 + r_{\text{theor}} + r_{\text{vol}})/3 = 2.7 \text{ \AA}. \quad (6)$$

The r_{theor} is the so-called kinetic radius of the molecule and r_{vol} is the radius obtained from summing up the volume elements of the molecule.

The resultant mean value of the radius $\bar{r}_0 = 2.7 \text{ \AA}$ determines the mean value of the specific volume of a 2-methyl-1-propanol molecule as, $\bar{V}_0 = 82.4 \text{ \AA}^3$. Table 1 presents the values of the specific radii and volumes of 2-methyl-1-propanol molecule and, for the sake of comparison, 2-methyl-2-propanol molecule (Mikusińska-Planner 1986).

3. Configuration of molecules in liquid 2-methyl-1-propanol

Assuming the model of intermolecular interaction in liquid 2-methyl-1-propanol proposed by Mikusińska-Planner (1979) we can show schematically the chain arrangement of molecules associated in the way presented in figure 2a*. The central molecule A is connected by a hydrogen bond of a length of $R_{\text{OH}\dots\text{O}} = 2.65 \text{ \AA}$ with the

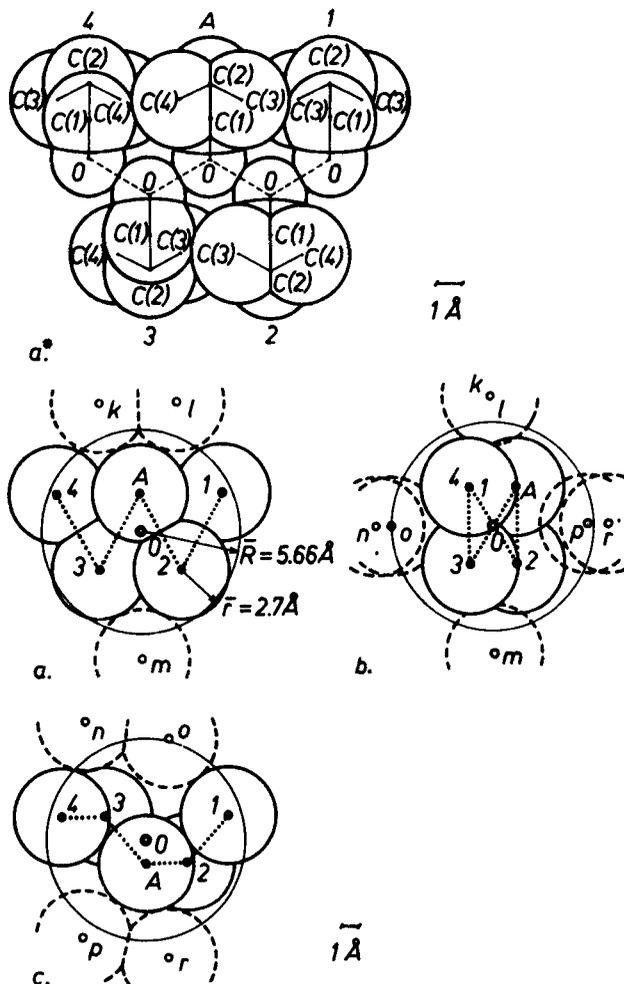


Figure 2. A model of liquid 2-methyl-1-propanol structure projected onto three orthogonal planes a*) projection on the plane of the figure in which the O and C(1) atoms lie a) projection on the plane of the figure which is parallel to the plane determined by the centres of molecules 1, 3, 4 etc. b) and c) projections where the centres of molecules 1, 3 and 4 determined a plane perpendicular to the plane of the figure.

molecules 2 and 3. The molecules A, 1, 2, 3 and 4 form an open chain with a mean angle of 120° between the OH...O bonds. The molecules 1 and 4 have $\text{CH}(\text{CH}_3)_2$ groups inclined to the plane containing the atoms O and C(1) in the direction opposite to the A molecule. The arrangement of associated molecules in a chain shown in figure 2a* may be illustrated in a simplified way. In figure 2a (and b, c) the molecules are shown as spheres of a radius $\bar{r}_0 = 2.7 \text{ \AA}$. In this figure the centres of molecules making a chain are linked with dotted lines. The molecules denoted by A and 2 in the projection a) lie above the plane of the figure whereas the centres of the molecules 1, 3 and 4 lie in this plane. The centre of the associate was assumed to be at O. From this point we drew a circle of the radius \bar{R} equal to the radius of the first coordination sphere. The value of the latter radius was obtained from (2) for $s(\text{max}) = 1.295 \text{ \AA}^{-1}$ (Mikusińska-Planner 1979) and is, $\bar{R} \approx 5.66 \text{ \AA}$. Since \bar{R} determines the volume of

an elementary pseudocell, we have, $\bar{V} = 759.5 \text{ \AA}^3$. Since the sphere of the radius $R = 5.66 \text{ \AA}$ comprises the centres of molecules 1, 2, A, 3 and 4, the projections were drawn only for 5 molecules. Molecules belonging to the neighbouring chaotically distributed associates are denoted in figure 2 broken lines. The centres of adjacent molecules are denoted by small letters k, l, m, n, o, p, r .

4. Molecule packing coefficient

The molecule packing coefficient, k , is defined, according to (3). The specific volumes of molecules of 2-methyl-1-propanol and 2-methyl-2-propanol are already known and given in table 1.

To find the coefficient k , we should also know the number of molecules in the known volume \bar{V} of an elementary pseudocell. This number x may be estimated from (3) which may be rewritten as

$$x = k(\bar{V}/\bar{V}_0). \quad (7)$$

The values of x obtained from (7) for the pseudocell volume $\bar{V} = 759.5 \text{ \AA}^3$ and the mean specific volume of a molecule $\bar{V}_0 = 82.4 \text{ \AA}^3$ together with the k values corresponding to the liquid phase, are given in table 2. For the sake of comparison, table 2 also includes the corresponding data for liquid 2-methyl-2-propanol taken from Mikusińska-Planner's (1986) paper.

Considering figure 2 and the data of table 2 on liquid 2-methyl-1-propanol we may expect that the coefficient k falls within the range $0.54 \leq k \leq 0.55$, as the number of molecules in the elementary pseudocell is $x = 5$. This supposition has been supported by the analysis of the areas of orthogonal projections of the associate on the plane limited by the radius \bar{R} of the elementary pseudocell (figure 2). The appropriate data for liquid 2-methyl-1-propanol are given in table 3, according to which, the area of the projection that does not fall within the borders of an elementary pseudocell makes 18.9% of the area of projection a) and 19.6% of the area of projection c) of the whole model of the associate of 5 molecules. So an average 19.2% of the area of projection of the model does not fall within the elementary pseudocell. However, the unoccupied space of the pseudocell above and below the model on the projection c) (figure 2c) may be filled with the molecules k, l, m, n, o, p, r of the neighbouring associates, according to figure 2. The areas of the projections of the molecules falling within the area of the pseudocell (table 3) make, on the average, about 17.5% of the area of projection of the model.

Thus, the area of projection of the elementary pseudocell of the volume $\bar{V} = 759.5 \text{ \AA}^3$ includes 80.8% of the area of projection of the model and 17.5% of the area due to the

Table 2. Number of molecules x of liquid 2-methyl-1-propanol and 2-methyl-2-propanol comprised in an appropriate elementary pseudocell for the admissible packing coefficients.

k	0.51	0.52	0.53	0.54	0.55	0.56	0.57	0.58
$x_{(\text{CH}_3)_2\text{CHCH}_2\text{OH}}$	4.70	4.79	4.88	4.97	5.06	5.16	5.25	5.34
$x_{(\text{CH}_3)_2\text{COH}}$	3.39	3.46	3.52	3.59	3.66	3.72	3.79	3.86

Table 3. Areas of the orthogonal projections of the model of liquid 2-methyl-1-propanol associates.

Orthogonal projection of 2-methyl-1-propanol associate model	Areas [Å ²]		
	<i>a</i>	<i>b</i>	<i>c</i>
The projection of the model of 5-molecule associate	110.0	68.0	81.6
The part beyond the borders of the pseudocell area	20.8	—	16.0
The projections of neighbouring associates falling into the area of the pseudocell	9.2		21.6

molecules *k, l, m, n, o, p, r* belonging to the neighbouring associates. Altogether it makes 98.3% of the total area of projections required for $x = 5$. The unfilled area making only 1.7% of the total area of the projection can be easily filled by molecules of the vacancy of the structure shown in figure 2b. Thus, consistent with previous suppositions we assume that the molecule packing coefficient $k = 0.55$ as the elementary pseudocell comprises 5 molecules of liquid 2-methyl-1-propanol.

5. Discussion

The value of packing coefficient obtained ($k = 0.55$) corresponds to the chain structure of associates of liquid 2-methyl-1-propanol. Moreover, a comparison between figures 3a and 3b proves that the chain structure of this compound requires more compact arrangement of molecules than in 2-methyl-2-propanol (figure 3b) (Mikusińska-Planner 1983). This results in a denser filling of a pseudocell with 2-methyl-1-propanol molecules when compared to that of 2-methyl-2-propanol. This is a direct consequence of the fact that $x_{(\text{CH}_3)_2\text{CHCH}_2\text{OH}} > x_{(\text{CH}_3)_2\text{COH}}$, as the packing coefficient for 2-methyl-2-propanol was found to be $k = 0.54$. According to table 2, this value corresponds to $x = 3.6$ molecules and as we have shown above, for 2-methyl-1-propanol this value is $x = 5$ molecules.

Determination of the packing coefficient is of great practical importance as it helps to find the right molecular liquid structure. For the sake of illustration let us assume the chain structure of liquid 2-methyl-2-propanol which is in contradiction with the results of Mikusińska-Planner (1983). Figure 3c presents an orthogonal projection of the assumed model onto the plane of the figure which corresponds to the projection of the 2-methyl-1-propanol model shown in figures 2a and 3a.

Orthogonal projections of these models are made for the characteristic parameters of individual liquid. For 2-methyl-2-propanol these parameters are $\bar{r}_0 = 3.03 \text{ \AA}$ and $\bar{R} = 5.7 \text{ \AA}$, after Mikusińska-Planner (1986). The OH...O bond length in the assumed associate would be $\bar{R}_{\text{OH}\dots\text{O}} = 2.8 \text{ \AA}$ and the angle between the directions of the bonds is 120° . As seen from table 2, the maximum number of 2-methyl-2-propanol molecules in the elementary pseudocell is $x = 3.86$. On the other hand, for the assumed chain structure of this alcohol $x > 4$ which follows directly from the analysis of the projection in figure 3c and from its comparison with the corresponding projection for 2-methyl-1-propanol (figure 2 and 3a). According to table 2, the value $x > 4$ would

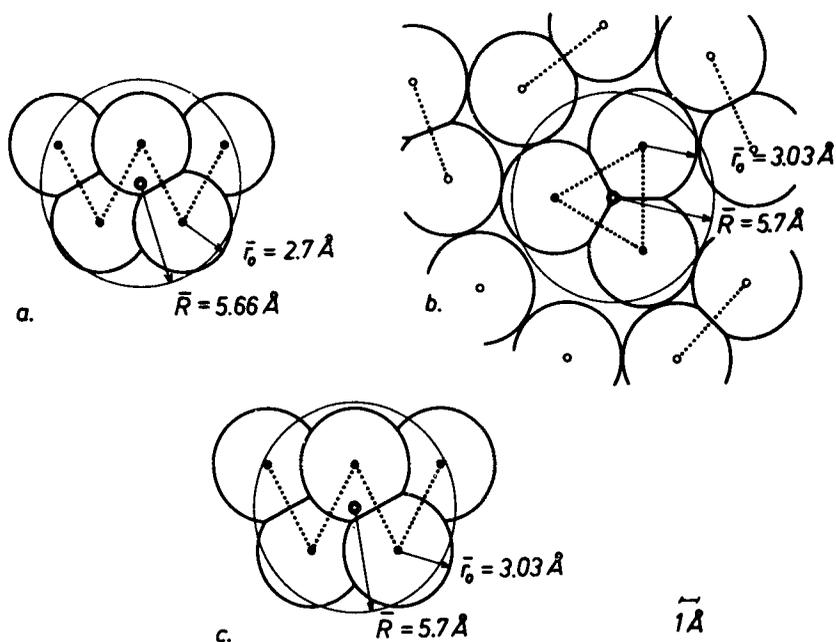


Figure 3. Molecule packing in an elementary pseudocell a) Molecules of the chain associate packed into an elementary pseudocell of 2-methyl-1-propanol b) Molecules of binary and triple associates packed into an elementary pseudocell of 2-methyl-2-propanol c) Molecules of the assumed chain associate packed into a pseudocell of 2-methyl-2-propanol.

give $k > 0.58$ which is beyond the liquid phase range. This analysis shows that the packing coefficient value found on the grounds of the liquid structure determined by X-ray diffraction studies is unquestionably and important criterion of correctness of the structure determination.

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