

The Structure of Liquids

III *. Diatomic Molecules

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When gases consisting of diatomic molecules, like oxygen, nitrogen and chlorine, are condensed to liquids, it might be expected that their molecules persist also in the liquid state and form the basic elements of the structure of the liquids. The experimentally determined atomic distribution curves for oxygen, nitrogen and chlorine seem, however, if they are correct, to indicate a rather complex structure¹⁻³.

Sharrah and Gingrich have determined atomic distribution curves for liquid oxygen at 62° K and 89° K¹, and the two curves show a marked resemblance. The main difference is a marked flattening of the maxima observed at 89° K compared with the corresponding maxima at 62° K.

In the atomic distribution curve for oxygen at 89° K peaks are observed at:

1.3 2.2 3.4 4.2 5.0 6.0 and 7.0 Å

Sharrah and Gingrich admit that the interpretation of some of these peaks, if real, is somewhat difficult. They suggest as a possible explanation the presence of ozone in the sample, produced by the strong X-ray irradiation of the liquid. As another possibility they mention the occurrence of O₄ molecules. The authors point out that the peak observed at 3.4 Å may have some relation to the distance of 3.48 Å between O₂ molecules in double-molecules, reported by Vegard⁴ to be present in the γ -form of crystalline oxygen.

Recently Kanda and Suguwara⁵ have shown that ozone is not produced in significant quantities, and as the experimental X-ray intensity curve is determined for a limited range of s values ($s = 4\pi \sin \theta/\lambda$), an error is introduced which may account for the maximum at 2.2 Å.

The distances between neighbouring peaks in the atomic distribution curve are:

0.9 1.2 0.8 0.8 1.0 and 1.0 Å.

The maxima are therefore approximately periodic, and their mean distance is 0.95 Å. This seems to indicate the presence of a very marked general ripple. If this is the case, a peak should be found at about 0.24 Å. This part of the

* Parts I and II: see reference 7.

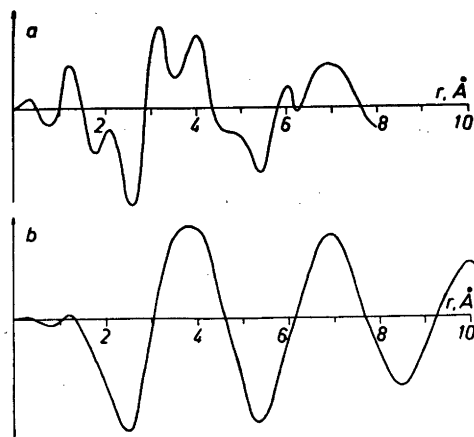


Fig. 1. Liquid oxygen.

- a. Atomic distribution curve. $4\pi r^2(\rho(r) - \rho_0)$.
 b. Electronic distribution curve. $\sigma(r)$.

curve is unfortunately not given in the publication. A computation of the inner part was therefore undertaken, using the intensity curve published by Sharrah and Gingrich. The result is given in Fig. 1 a, and from this curve it is seen that a maximum is really found between 0.2 and 0.3 Å. A period of the general ripple, $p_r = 0.95$ Å, should correspond to an error in the intensity curve at $s = 2\pi/p_r = 6.6$ Å⁻¹ or $\sin \Theta/\lambda = 0.53$. The occurrence of a maximum at 0.2–0.3 Å in the atomic distribution curve indicates that this error should be positive. The intensity curve of Sharrah and Gingrich really possesses a small maximum at about $\sin \Theta/\lambda = 0.53$ Å. It is therefore quite likely that the effect of a relative small positive error here is sufficiently increased to account for the observed general ripple by the introduction of the factor $1/f^2$.

An electronic distribution curve for oxygen at 89° K has been computed from the intensity curve of Sharrah and Gingrich. The result is given in Fig. 1 b.

Both curves of Fig. 1 represent the difference between the actual density of the liquid, and a uniform electronic, respectively atomic density of the sample.

A comparison reveals that curve 1 a must contain a term of period 0.95 Å. The amplitude of this term falls off with increasing r . For very small values of r it also seems to decrease, and the maximum expected at 0.24 Å is shifted a little towards greater r -values. The atomic distribution is computed from the equation^{1,6}:

$$4\pi r^2(\rho(r) - \rho_0) = \frac{2r}{\pi} \int_0^{s_0} s \cdot i(s) \cdot \sin(rs) \cdot ds$$

where $i(s)$ is derived from the experimental data, s_0 is the upper limit of the determined intensity range, $\rho(r)$ is the actual atomic density, and ρ_0 is the average atomic density. It is readily seen that the general ripple may be caused

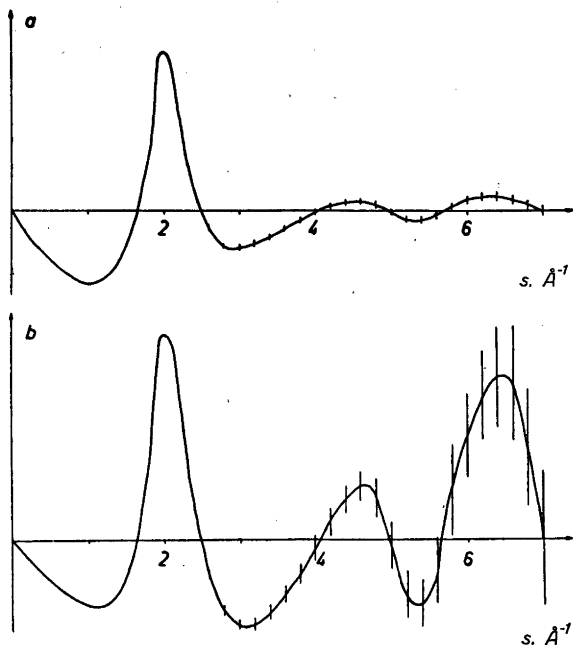


Fig. 2. Intensity curves for liquid oxygen.

a. $s \cdot I_{m+l}(s)$

b. $s \cdot i(s)$

by a comparatively broad maximum at about $s = 6.6 \text{ \AA}^{-1}$ in the intensity curve. A certain width of this maximum is required to make the amplitude decrease with increasing r . The reduction of the amplitude and shifting of the position of the first maximum to greater values of r are effected by the factor r on the right side of the above equation.

A positive error in the intensity-curve at about $s = 6.6 \text{ \AA}^{-1}$ will therefore well account for the general ripple of the atomic distribution curve.

Fig. 2 a represents the term $s \cdot I_{m+l}(s)$ from which the electronic distribution is computed. $I_{m+l}(s)$ is obtained from ⁷:

$$I_{m+l}(s) = I_{\text{corr}}(s) - I_B(s)$$

where $I_{\text{corr}}(s)$ is the corrected experimentally determined intensity, and $I_B(s)$ is the sum of the coherent and incoherent scattering from the oxygen atoms.

Fig. 2 b represents $s \cdot i(s)$ from which the atomic distribution is computed. This term is given by:

$$s \cdot i(s) = s \cdot I_{m+l}(s) / f^2$$

where f is the atomic scattering factor.

The vertical lines in the curves indicate the influence of a small, constant error in $I_{m+l}(s)$.

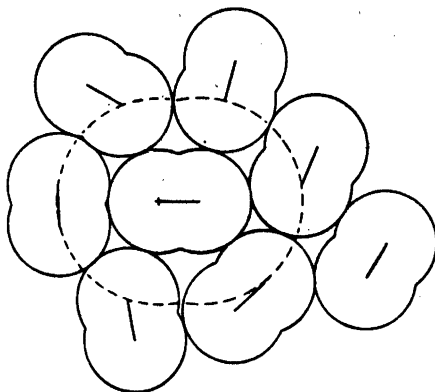


Fig. 3. 2-dimensional packing of "diatomic molecules".

In curve 2 b the magnitude and width of the maximum at $s = 6.6 \text{ \AA}^{-1}$ are very great. It is readily seen that a small experimental error may greatly influence the computation of the atomic distribution curve.

It is most likely that a strong general ripple, deforming the atomic distribution curve, has made an interpretation of the structure rather problematic.

The electronic distribution curve 1 b is very simple; it has only three maxima in the interval of 0—8 Å. The first one is a quite small and sharp peak at 1.23 Å. The next maximum has a great width, from about 3.0 to 4.5 Å, and the top is unusually flattened. The third peak is located at about 6.9 Å.

The position of the first maximum corresponds well to the spectroscopically observed distance between the atoms in the oxygen molecule, 1.22 Å.

From X-ray crystallographic data it is known that the distance between oxygen atoms in direct contact but not bounded together, is about 3.1—3.2 Å. The peak between 3.0 and 4.5 Å is therefore, as indicated in Fig. 3, due to distances between the nearest neighbours of oxygen molecules.

The third peak, at 6.9 Å, probably represents the second peak caused by packing of the oxygen molecules. Assuming the ratio between the distances to the first and second neighbours in the packing of oxygen molecules to be the same as in molten metals and liquid inert gases, between 1.8 and 1.9, the position of the first peak caused by the packing should be 3.6—3.8 Å, when the second one is found at 6.9 Å. The actual position of the second and greatest peak in the distribution curve is at about 3.8 Å.

The diatomic oxygen molecules may then, as a first rather rough approximation, be considered as spheres. It should therefore be necessary to consider the properties of the systems formed when solid spheres are packed together, before a more detailed discussion of the structure of liquid oxygen is attempted.

The atomic and electronic distribution curves for liquid nitrogen shown in Fig. 4 have been computed from an experimental intensity curve given by Sharrah². The atomic distribution curve, Fig. 4 a, seems to contain a term of period *ca.* 1 Å. The electronic distribution curve has only three maxima.

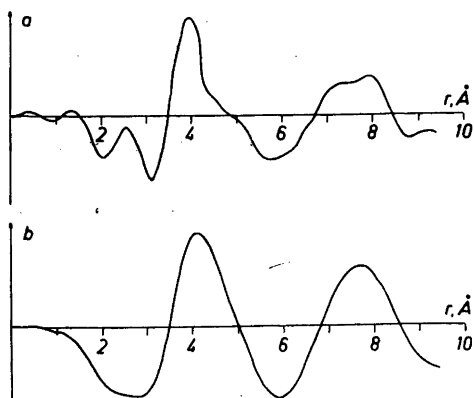


Fig. 4. Liquid nitrogen.

- a. Atomic distribution curve. $4\pi r^2 (\rho(r) - \rho_0)$.
 b. Electronic distribution curve. $\sigma(r)$.

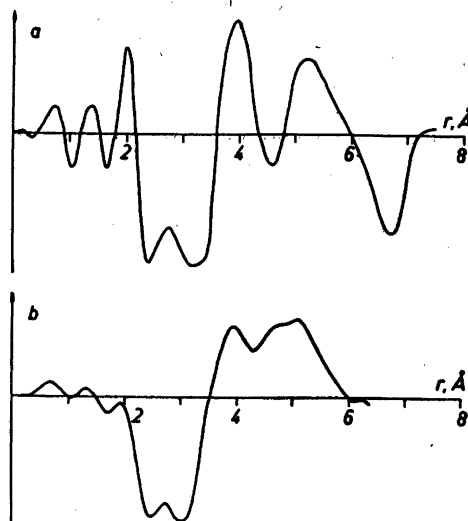


Fig. 5. Liquid chlorine.

- a. Atomic distribution curve. $4\pi r^2 (\rho(r) - \rho_0)$.
 b. Electronic distribution curve. $\sigma(r)$.

The first maximum between 1.0 and 1.54 Å is very small, and probably represents the intramolecular distance, while the two larger maxima at 4.1 and 7.7 Å represent the first and second packing distances as previously seen by oxygen. The ratio of the distances is 1.88, corresponding to a packing of spheres.

The distribution curves for liquid chlorine shown in Fig. 5 have been computed from an experimental intensity curve given by Gamertsfelder³. Both curves contain ripple terms and no attempt of interpretation has been made.

From the three above examples it is seen that the existing experimental X-ray scattering data for liquid diatomic molecules are quite unsatisfactory for determination of correct atomic distribution curves. This seems to be caused in part by the limited s -range and in part by insufficient accuracy of the data at even moderate s -values. In most cases, however, it is possible to compute an electronic distribution curve, the interpretation of which is rather simple.

SUMMARY

The two preceding papers of this series deal with systematic errors in the distribution curves of monoatomic liquids. In this paper the distribution curves of diatomic molecules are considered, using liquid oxygen, nitrogen, and chlorine as examples. It is shown how the atomic distribution curves emphasize the systematic errors compared with the electronic distribution curves.

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