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Thermal neutron diffraction from the liquids N₂ and O₂. Determination of nearest neighbor parameters and angular correlations

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Using a double axis crystal spectrometer, we have determined the structure factor $S(\kappa)$ of the liquids N₂ and O₂ up to a maximum wavevector $\kappa_m = 11 \text{ \AA}^{-1}$. We derive the parameters characterizing the first nearest neighbor shell and find that the intramolecular bond length is well determined, whereas the width and the volume of the shell is derived with rather large uncertainties. We also demonstrate how our data analysis program may be used to give necessary limits for κ_m , dependent upon which parameters are to be determined. Finally, we deduce the angular correlations which give a result consistent with the dominant quadrupolar and dipolar interactions in N₂ and O₂, respectively.

I. INTRODUCTION

Neutron diffraction plays an important role in structure determinations of atomic and molecular liquids. Until recently, the diffraction was limited to wave vector transfers not larger than a maximum of $\kappa_m = 10\text{--}15 \text{ \AA}^{-1}$ [$\kappa = (4\pi/\lambda) \sin(\theta/2)$, where θ is the scattering angle and $\lambda = 2\pi/k$ is the wavelength of the incident neutrons]. With the occurrence of epithermal neutrons, this range has been extended significantly, which at least in principle, improves the reliability of the structural information gained from the experiment. However, since there are also problems involved in determining the structure accurately from measurements with epithermal neutrons, it seems worthwhile investigating which aspects of the structure of molecular liquids are well determined by each specific technique. To elucidate this problem, we have performed neutron diffraction from the two liquids N₂ and O₂ using thermal neutrons giving a $\kappa_m \approx 11 \text{ \AA}^{-1}$.

We have attached particular importance to the accuracy that can be expected in determinations of intramolecular bond lengths (d) and vibrational amplitudes (σ). We shall show, using the method of analysis reported by Yssing Hansen and Carneiro,¹ that the bond length can be well determined.

Two extensions to the procedure of Ref. 1 were made. Firstly, since the liquids were contained in an Al cylinder, particular care had to be taken in order to obtain a reliable background subtraction. This was accomplished by calculating the transmission through the different volume elements of the sample liquid, and then correcting the scattering from the cylinder for the shielding. Secondly, the paramagnetic scattering was subtracted from the scattering data in the same way as done by Dore *et al.*²

II. THEORY

The relation between the scattered intensities $I(\lambda, \kappa)$ and the structure factor $S(\kappa)$ takes the form

$$I(\lambda, \kappa) = A(\lambda) T(\lambda, \kappa) \left\{ S(\kappa) + f_p(\lambda, \kappa) + \frac{\sigma_{\text{inc}}}{\sigma_{\infty}} [1 + f_p(\lambda, \kappa)] + \frac{\sigma_m(\lambda)}{\sigma_{\infty}} \right\}, \quad (1)$$

where $T(\lambda, \kappa)$ is the transmission coefficient; A is a normalization constant; σ_{inc} , σ_{∞} , and σ_m are the incoherent, coherent, and multiple scattering cross sections, respectively; and $f_p(\lambda, \kappa)$ is the Placzek correction. This latter correction may approximately be written³

$$f_p(\lambda, \kappa) = \left(\frac{k_B T}{2E} - \frac{\kappa^2}{k^2} \right) \left(\frac{m}{M} \right) + \left(\frac{1}{2} \frac{\kappa^2}{k^2} + \frac{3}{8} \frac{\kappa^4}{k^4} \right) \left(\frac{m}{M} \right)^2 + \dots, \quad (2)$$

where T is the temperature, k_B the Boltzmann constant, $E (= \hbar^2 k^2 / 2m)$ is the energy of the neutrons, m the neutron mass, and M the mass of the scatterer. $f_p(\lambda, \kappa)$ is shown in Fig. 1 for $M = 16.8$ at $k = 3.73$ and 6.74 \AA^{-1} . This corresponds to our experimental setup for nitrogen, taking the effective mass⁴ of the N₂ molecule to be $M = 16.8 m$. Also shown is the Placzek correction for an equivalent time of flight (TOF) experiment ($\theta = 90^\circ$). It is seen that the Placzek correction is smaller for the double axis spectrometer (DAS) for small κ values. At $\kappa \approx 3 \text{ \AA}^{-1}$, it becomes constant for the TOF case while f_p continues to increase for the DAS case. This leads in the DAS case to the dilemma that, while we want to go to large κ 's to get adequate structural information, at such wave vectors the Placzek correction gets progressively more difficult to account for. As we shall discuss below, a consequence of this dilemma appears to be that parts of the structural information is best illuminated at at modest κ 's, whereas other parts are clearly best determined by larger wave vectors. The relation between the structure factor $S(\kappa)$ and the pair correlation function $g(r)$ is given by

$$4\pi r \rho_0 [g(r) - 1] = \frac{2}{\pi} \int_0^\infty \kappa [S(\kappa) - 1] \sin(\kappa r) d\kappa, \quad (3)$$

where ρ_0 is the number density of the matter.

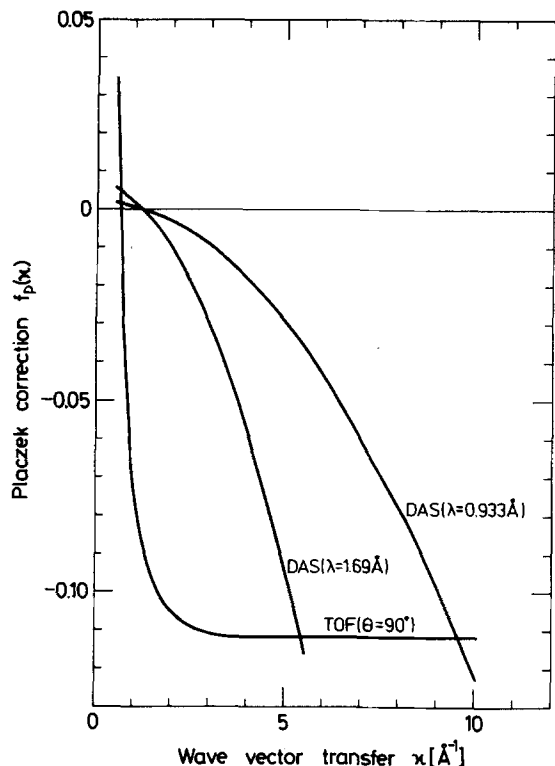


FIG. 1. Placzek correction to the structure factor of N₂ when double axis crystal diffraction (DAS) or time of flight (TOF) techniques are used. In the case of DAS, we have taken the parameters from our experiments.

In order to extract information about the details of $g(r)$ at small r 's, in our case of diatomic liquids the bond length d and the vibrational amplitude σ of the intramolecular bond, when $S(\kappa)$ is only measured up to a finite κ_m , and model pair correlation function $g^m(r)$ is introduced. It seems that the pair correlation function at small r 's describes a well-defined neighbor

$$g^m(r) = \frac{1}{4\pi r \rho_0} \frac{N}{d\sqrt{2\pi\sigma^2}} \exp\left(-\frac{(r-d)^2}{2\sigma^2}\right) \quad (r \text{ small}), \quad (4)$$

where the neighbor shell is characterized by N , d , and σ . From Eq. (4), a model structure factor is obtained:

$$S^m(\kappa) = 1 + N \frac{\sin(\kappa d)}{\kappa d} \exp\left(-\frac{1}{2}\sigma^2\kappa^2\right) \quad (\kappa \text{ large}). \quad (5)$$

Assuming that $S^m(\kappa) = S(\kappa)$ for the largest measured κ values, the shell parameters can be determined from the experimental $S(\kappa)$. In our case with diatomic molecules, we only need to consider one neighbor shell in $g^m(r)$ since all other features of $g(r)$ are directly determined from the measurements. To ensure that this was really the case, we parameterized $g(r)$ in terms of a second and third nearest neighbor shell as prescribed in Ref. 1, and found as expected that our conclusions concerning d and σ were not influenced by the details of how those two neighbor shells were parameterized.

III. EXPERIMENTAL

The measurements were performed at a double axis spectrometer at the DR3 reactor at the Research Establishment Risø. We employed two different incoming

wave vectors $k_1 = 3.725 \text{ \AA}^{-1}$ ($\lambda_1 = 1.687$) and $k_2 = 6.736 \text{ \AA}^{-1}$ ($\lambda_2 = 0.933$) using a Ge and Be monochromator, respectively, at a fixed scattering angle $2\theta_M = 30^\circ$. The scattering angle θ was varied between 3° and 117° . We used soller slit collimation before and after the sample which gave an angular resolution of 1° FWHM. The sample chamber consisted of a vertical aluminum cylinder with an inner radius of 6.5 mm subdivided by horizontal Cd plates in order to reduce the multiple scattering, the distance between the plates being 5 mm. The chamber was cooled by pumping on liquid nitrogen contained in a double Dewar cryostat. We used $\sigma_{co} = 11.1$ and 4.23 barn for N₂ and O₂, respectively. From Blech and Averbach,⁵ we calculated $\sigma_m = 0.47$ and 1.5 barn in the two cases. σ_{inc} was set to zero for O₂ and to 0.3 barn for N₂.

IV. NEAREST NEIGHBOR PARAMETERS

The measured intensity data for nitrogen and oxygen are shown in Fig. 2 together with the intensity data for the empty Al cylinder. When determining $S(\kappa)$ from Eq. (1), we tried several different values for the effective mass, ranging from the atomic mass to the molecular mass. The corresponding change in $S(\kappa)$ was insignificant for our purpose. The deduced structure factors are shown in Figs. 3 and 4 together with the structure factors determined by Dore *et al.*

First, it should be noted that our structure factor does contain spurious oscillations at $\kappa = 2.7$, 3.1, and 4.4 \AA^{-1} , which corresponds to the strongest Al reflection, as seen in Fig. 2. From this point of view, it would clearly be advantageous to use a vanadium cell, since Va does not scatter neutrons coherently. However, for our purpose, to determine the bond length by thermal neutrons, we want to demonstrate that our background subtraction procedure suppresses the Al peak to approximately 3%. Therefore, the weak structure in the empty cell data at κ 's larger than 5 \AA^{-1} is not of importance for our determination of d . Further, we want to point out that although we could have used a Va cell to our advantage, one of the interesting applications of our method would be to investigate changes of molecular bond length with pressure. And using high pressure cells, one cannot avoid materials which will give structure in the neutron diffraction pattern.

Besides this artificial structure in our $S(\kappa)$, the overall discrepancy between our results and those of Ref. 2 at smaller wave vectors is noteworthy. In this respect, it is important that the Placzek correction $f_p(\kappa, \lambda)$ was not carried out in Ref. 2, and since $f_p(\kappa, \lambda)$ has the same magnitude as the discrepancy, it is likely that part of it is owing to differences in the data treatment. The reason why $f_p(\kappa, \lambda)$ does not seem to influence $S(\kappa)$ at larger wave vectors in Ref. 2 is that the limiting value of $S(\kappa) - 1$ was employed in both cases.

We now turn to our major concern in this paper, namely, how well d and σ can be determined from our measurements. In Table I are shown our parameters from a best fit obtained as described above for the liquids N₂ and O₂ and they are compared to "expected"

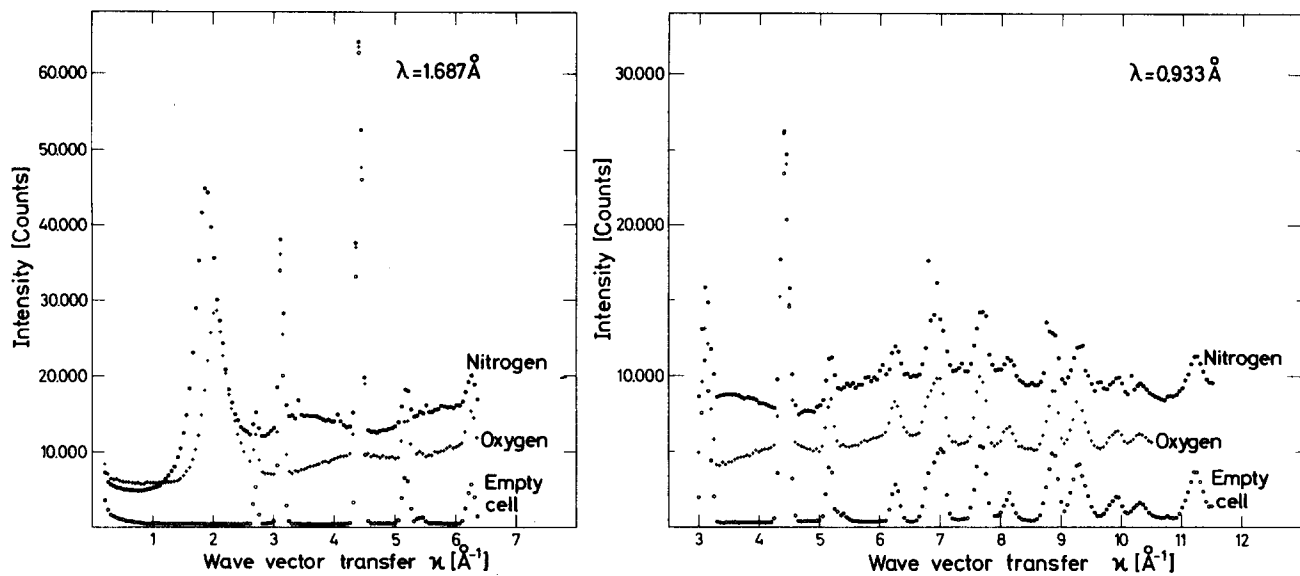


FIG. 2. Measured intensity data from the empty cell and the cell filled with liquid O₂ and liquid N₂.

values as deduced from other measurements or calculations. The expected value for the bond length d is taken from optical data,⁸ σ is taken to be the value calculated by Cyvin,⁷ whereas N is taken to be

$$N = \left(1 + \frac{\sigma}{d}\right)^{-1}, \quad (6)$$

which ensures that the number of nearest neighbors is unity. We found that the fit was sensitive to d but only weakly dependent on σ and N , and accordingly it appears from Table I that d is well determined for both liquids by our procedure, whereas the agreement for the parameters σ and N is poorer. Apart from their influence on the fit, we would like to point out how well a

given parameter in Eq. (4) is determined given a maximum experimental wave vector κ_m . By inspection of Eq. (5), we see that d enters via the expression

$$\sin(\kappa d)/\kappa d. \quad (7)$$

Since, in principle, it requires one half-period to determine a sine function, the critical maximum wave vector in this respect is $\kappa_m = \pi/d \approx 3 \text{ \AA}^{-1}$. Therefore, it is not astonishing that we get a good determination of d with our $\kappa_m = 11 \text{ \AA}^{-1}$. If we similarly inspect Eq. (5), σ is determined by the term

$$e^{-(1/2)\sigma^2\kappa^2}, \quad (8)$$

and if we require that the argument should be unity for

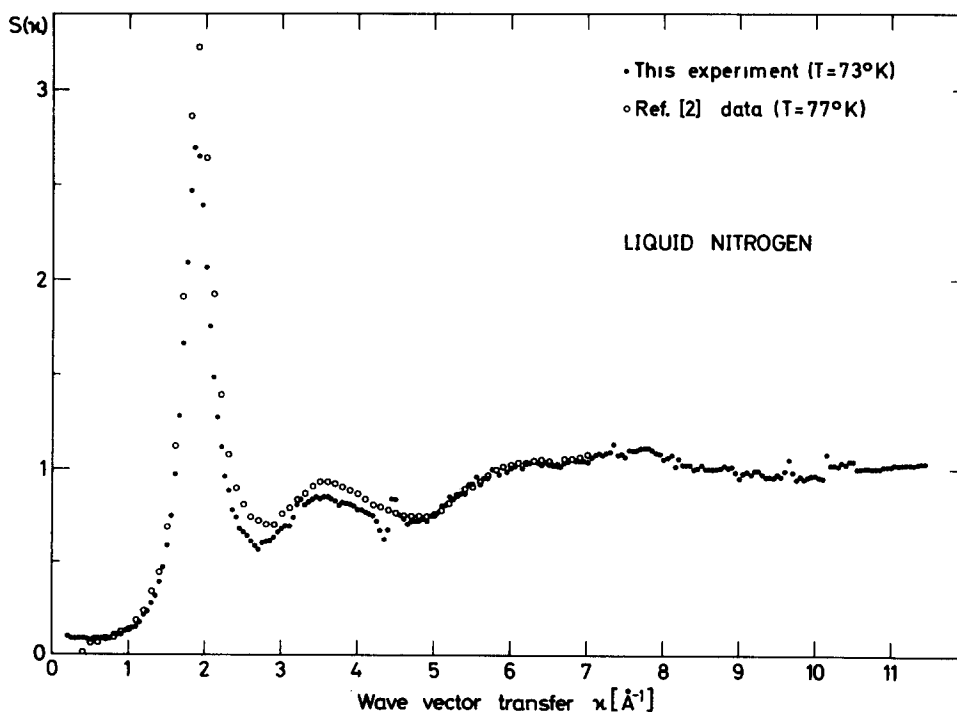


FIG. 3. Structure factor $S(\kappa)$ for liquid N₂ at $T = 73 \text{ K}$, as obtained from our experiment (\bullet) and from Ref. 2 at $T = 77 \text{ K}$ (\circ).

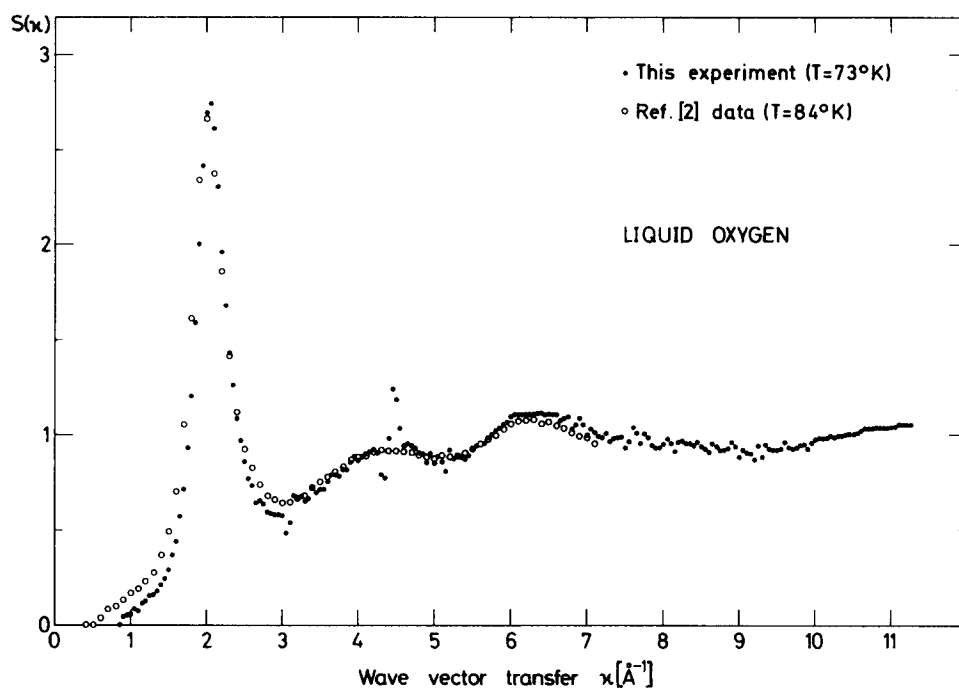


FIG. 4. Structure factor $S(\kappa)$ for liquid O₂ at $T=73$ K as obtained from our experiment (\bullet) and from Ref. 2 at $T=77$ K (\circ).

a good description of the experimental function, we get here a critical value $\kappa_m = \sigma^{-1}\sqrt{2} \approx 50 \text{ \AA}^{-1}$, much larger than our maximum wave vector. Finally, regarding the accuracy of the determination of N , it is easiest to look at Eqs. (4) and (7), which demonstrate that the area of the first neighbor peak gives this number after correction for the small ratio σ/d . Consequently, artificial effects in $g(r)$ originating from small insufficiencies in our data treatment can give rather large errors in N .

Our model analysis, as well as our fitting procedure, therefore shows that the bond length is well determined, whereas accurate values for σ and N requires appreciably more elaborate experiments and data treatment. We find that this is in accordance with earlier experiments where a reliable value for σ was found using $\kappa_m = 35 \text{ \AA}^{-1}$.⁸

V. ANGULAR CORRELATIONS

An interesting difference between the interaction between N₂ and O₂ molecules is that, in N₂, quadrupole forces dominate as opposed to O₂ where dipolar forces

TABLE I. Molecular bond lengths d and vibrational amplitude σ for the liquids N₂ and O₂, as determined from neutron diffraction with a maximum wave vector $\kappa_m = 11 \text{ \AA}^{-1}$. N is defined by Eq. (4). The origins of the expected values are described in the text.

	N ₂		O ₂	
	This work	Expected values	This work	Expected values
d	1.082	1.094	1.219	1.207
σ	0.1007	0.032	0.0222	0.037
N	0.9056	0.97	0.7880	0.96

are most important. Therefore, N₂ crystallizes in the $Pa3$ structure where the molecules are predominantly perpendicular, whereas O₂ has its molecules aligned in the low temperature α and β phases. To see whether this difference in angular correlations prevails in the liquid, Dore *et al.*² analyzed the structure factor in terms of different form factors for the different orientational correlations, but in this way no clear difference between N₂ and O₂ was seen.

By analyzing the pair correlation functions in terms of a maximum likelihood principle, we are, however, able to see distinct differences between the two liquids in accordance with their expected behavior. In Table II, we show the positions of the second and third maximum in $g(r)$ (r_2 and r_3 , respectively, for the liquids N₂ and O₂). The values are taken from a fit for the second and third neighbor shell similar to what is described above for the first neighbor shell. Our values are in reasonable agreement with those obtained by J. Dore *et al.*⁸ Based on the data of Table II, the positions most likely for the second and third nearest neighbor are shown in Figs. 5 and 6 for nitrogen and oxygen, respectively, and the shaded area indicates the volume within which a neighboring molecule is most likely to be situated with respect to the center molecule in the figures. Accordingly, we show some possible position of neighboring molecules with their nuclei placed on a

TABLE II. Second and third nearest neighbor distances in liquid N₂ and O₂, determined by the corresponding maxima in the pair correlation function.

Liquid	N ₂	O ₂
$d_2 (\text{\AA}^{-1})$	3.8	3.3
$d_3 (\text{\AA}^{-1})$	4.9	4.3

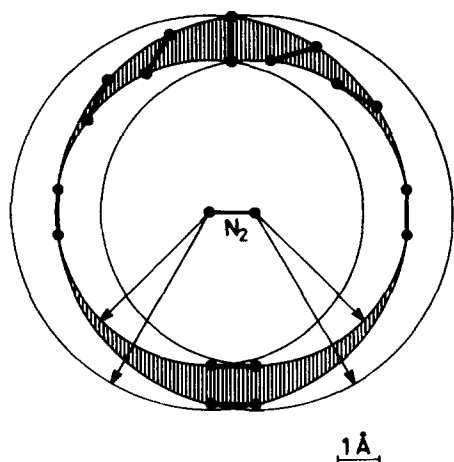


FIG. 5. Possible angular correlations in liquid N₂. The circles indicate loci of maximum probability for the positions of neighboring nuclei with respect to the two nuclei of the center molecule. The shaded area indicates the volume within which a neighboring molecule must be situated. Some examples of possible configurations are shown, as discussed in the text.

maximum probability circle. This reveals the following difference between N₂ and O₂. *Perpendicular* to both types of molecules (above and below in the figures), there is space for either parallel or perpendicular configuration; but only in the case of nitrogen can one place a neighbor molecule along the molecular axis of the center one, and that has to be oriented perpendicularly. This difference implies that if a most probable orientation between molecules exists, it must be perpendicular for nitrogen and parallel for oxygen, consistent with our picture of the dominant interactions. Thus, our analysis indicates that different angular correlations between the two types of molecules prevail in the liquid phase.

We find it interesting that our analysis, in case of liquid N₂, agrees quantitatively with the more rigorous results for the angular correlations obtained by Barojas *et al.*⁹

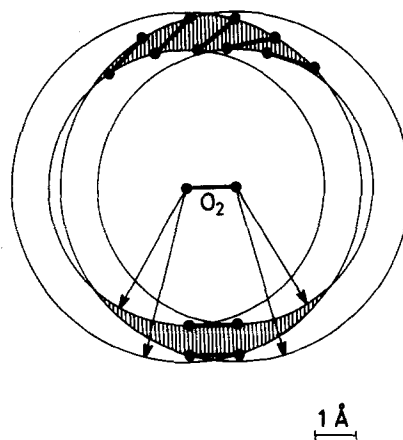


FIG. 6. Possible angular correlations in liquid O₂, as shown for liquid N₂ in Fig. 5.

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