

## Scattering of X Rays by Polyatomic Liquids. nHeptane

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Citation: *J. Chem. Phys.* **3**, 252 (1935); doi: 10.1063/1.1749649

View online: <http://dx.doi.org/10.1063/1.1749649>

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The article by Thorne Lay and Hiroo Kanamori is an excellent review of the energy release of the 1964 Chilean earthquake. The authors estimate that the earthquake released approximately five times as much energy as the atomic bomb dropped on Nagasaki. This is a very interesting comparison, but I believe the authors have underestimated the total strain energy release by a factor of about 3, or 10 times if one considers the energy released by the earthquake as a whole. The seismic energy released by the earthquake is estimated to be about 10<sup>17</sup> J, while the energy released by the atomic bomb was about 10<sup>16</sup> J. The authors also mention that the earthquake released energy equivalent to 100,000 atomic bombs. This is a very rough estimate, but it is interesting to see that the energy released by the earthquake is indeed much larger than the energy released by the atomic bomb. Despite the catastrophic damage potential of nuclear bombs, the forces of nature occasionally unleash much larger energy releases. Although the nuclear bombs are under our control, earthquakes, volcanic eruptions, and extreme weather events are not. However, by judicious preparation and avoidance measures, humans can significantly diminish the damage of natural events.

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By the act of hitting a ball with a bat, one calculates the force energy to deliver the ball to its new location, but one must also take into account that the ball extended its energy release to that which became struck by the ball as its momentum ceased and passed energy to the struck item. Therefore the parameters of the damage extend into the future when the received energy to that pushed upon, later becomes released in a new event. Perhaps calculations of one added that in, while another's calculations did not. E.M.C.  
Written by Edgar McCarroll, 14 July 2012 19:59

# Scattering of X-Rays by Polyatomic Liquids. *n*-Heptane

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(Received March 5, 1935)

A Fourier integral analysis of Katzoff's data for the x-ray scattering of *n*-heptane gives not only the arrangement of molecules in the liquid, but also the most probable distances within the single molecule. It is shown that the molecule consists of a zigzag carbon chain. Adjacent molecules are somewhat oriented and increase in temperature

makes a more random condition. The Fourier integral theorem is shown to be valid even though the function for which it is used does not converge within the limits of the data. The distribution function is used to calculate the intensity, giving a fair agreement with the experimental values.

RECENT publications<sup>1, 2</sup> in the field of x-ray scattering by liquids have led the writer to the questions:

- How much information concerning the structure of single molecules may be obtained from liquid scattering data?
- Is the use of the Fourier integral theorem valid for data extending over a small range of  $\sin \theta/\lambda$ ?

The data of Katzoff<sup>3</sup> for *n*-heptane have permitted calculations that furnish definite answers to the questions. These data are particularly excellent for they are taken with monochromatic x-rays, the absorption in the sample is determined, and they extend over a large angular range.

## THEORY

Zernike and Prins<sup>4</sup> and Debye and Menke<sup>5</sup> have developed equations for the x-ray scattering of atomic liquids in terms of a distribution function. Warren<sup>1</sup> and Zachariasen<sup>2</sup> have applied these in slightly modified form to the scattering of molecular liquids having atoms of equivalent scattering power. The Fourier integral theorem is used to solve these equations for the distribution function.

The fundamental scattering equation

$$I_{(\text{obs.})}/NTF^2 - 1 = (1/K) \int_0^\infty (q(r)/r) \sin Krd r \quad (1)$$

gives on transformation

$$q(r) = (2r/\pi) \int_0^\infty K(I_{(\text{obs.})}/NTF^2 - 1) \times \sin Krd K, \quad (2)$$

where:

$I_{(\text{obs.})}$  is the observed scattering, corrected for absorption, polarization and incoherent scattering;

$N$  is the number of irradiated atoms;

$T$  is the scattering per electron;

$F$  is the atomic scattering factor for the given value of  $K$ ;  $K$  is  $4\pi \sin \theta/\lambda$ , where  $\theta$  is half the scattering angle and  $\lambda$  is the wavelength;

$q(r)$  is the number of atoms in excess of the average lying at distance  $r$  Angstroms from a given atom;

$I_{(\text{obs.})}/NTF^2$  is for brevity denoted by  $E$ , in keeping with common usage.

Eq. (2) is identical in meaning with Eq. (2) of Katzoff's paper, since the average number of atoms at  $r$  is  $4\pi r^2 \rho$  ( $\rho$  is atoms per  $A^3$ ).

In practice the data do not extend to infinity, nor does  $K(E-1)$  converge at the largest obtainable values of  $K$ . The results, however, show that no great error is introduced by integrating from  $K=0$  to  $K=2\pi$ .

## METHOD OF CALCULATION

The  $E$ -curve is determined as shown in Fig. 1. Katzoff's intensity curves for *n*-heptane were replotted to a convenient scale and the calculated  $F^2$  and incoherent scattering curves drawn to the same scale. At the point  $s(2 \sin \theta/\lambda) = 1$ , it may be assumed that the atoms scatter independently and that the observed scattering is thus the sum of the independent coherent scattering plus the modified scattering. The point  $s=1$  was chosen because on the theoretical gas scattering curve it lies half-way between a maximum and a minimum. The procedure is not very exact for large  $s$  values because of uncertainty both in the  $F^2$  and

<sup>1</sup> B. E. Warren, *Phys. Rev.* **44**, 969 (1933).

<sup>2</sup> W. H. Zachariasen, *Phys. Rev.* **47**, 277 (1935).

<sup>3</sup> S. Katzoff, *J. Chem. Phys.* **2**, 841 (1934).

<sup>4</sup> F. Zernike and J. A. Prins, *Zeits. f. Physik* **41**, 184 (1927).

<sup>5</sup> P. Debye and H. Menke, *Physik. Zeits.* **31**, 797 (1930).

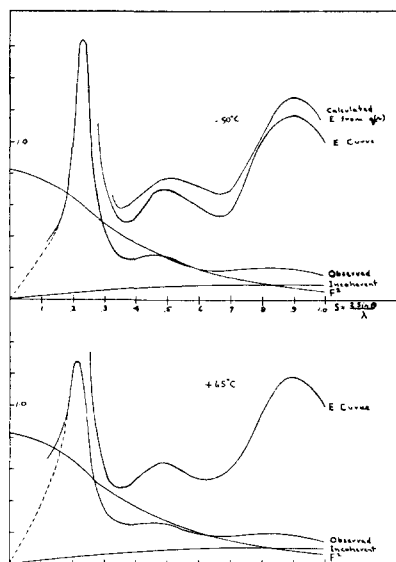


FIG. 1. Scattering curves for *n*-heptane (Katzoff);  $E$  curves and  $E$  curve calculated from  $q(r)$  curve.

the experimental curves, but subsequent calculations showed that the results were chiefly due to portions of the scattering curve at smaller  $s$  values where the accuracy is greater. James and Brindley's<sup>6</sup>  $F$  values were used for carbon and hydrogen. In the  $F^2$  curve the values are for  $C=Z=8$  and the hydrogen is neglected. The  $E$  curves are obtained by dividing the experimental curves by the  $F^2$  curves. Since both are in the same units,  $E$  is in absolute units.

Integration of Eq. (2) was carried out in 0.25Å steps for values of  $r$  from 0.25Å to 15Å. This laborious calculation was materially shortened by the use of a Coradi rolling sphere harmonic analyzer.<sup>7</sup> The function  $K(E-1)$  was plotted against  $K$ , (Fig. 2) and expressed as a Fourier series by tracing with the harmonic analyzer. The resulting expression for  $K(E-1)$  was multiplied by  $\sin Kr$  and each term integrated from  $K=0$  to  $K=2\pi$ . The corresponding  $q(r)$  curves are shown in Fig. 3.

<sup>6</sup> R. W. James and G. W. Brindley, *Phil. Mag.* **12**, 81 (1931).

<sup>7</sup> Available through the courtesy of Professor Henry Schultz of the Department of Economics, University of Chicago.

## DISCUSSION

The  $q(r)$  curves have unexpectedly sharp peaks at 1.4, 2.5, and 3.8Å. These peaks are due to the outer parts of the scattering curve, where the molecules scatter quite independently, and they undoubtedly show within experimental limits the most probable distances within a single molecule. This is verified by the slight change with temperature and by calculations made with an arbitrarily drawn  $K(E-1)$  curve which minimized the fluctuations at large  $K$  values. This curve (Fig. 2A) follows the  $-50^\circ$  curve to  $K=\pi$  and diverges in the range where the experimental uncertainty is greatest. It gives the distribution function of Fig. 3A. The peaks appear at the same  $r$ -values, but are much less pronounced. Since the experimental uncertainty is probably not as great as shown in the arbitrary curve the true distribution function probably lies between the two curves.

The  $q(r)$  peaks at larger distances show the concentration of scattering matter in adjacent molecules. The peak for the lower temperature curve is at  $r=4.5$  to 6.5Å, with a mean value of 5.25 to 5.5Å. This distance is somewhat greater than the mean diameter of the molecule because of the distribution of scattering atoms along the length of the adjacent molecule. At the higher temperature the peak extends outward, giving a mean value of about 5.75Å. Elevation of the temperature has only increased the amplitude of the molecular vibration and given a more disorderly arrangement.

The most probable distance ( $a$ ) of scattering atoms may be more directly determined, as shown by both Zachariasen and Warren, by application of the Ehrenfest-Keesom equation

$$\lambda/2 \sin \theta(\max) = d_{\text{Bragg}} = 0.814a.$$

The value so calculated from the major peak of the scattering curve is the same as given by the  $q(r)$  curve. Application of this equation to the second and third peaks gives distances of 2.54 and 1.43Å, respectively.

The radial distribution obtained does not imply the assumption of a structure for the liquid. Although they may be in random motion and orientation with respect to a given point, two adjacent

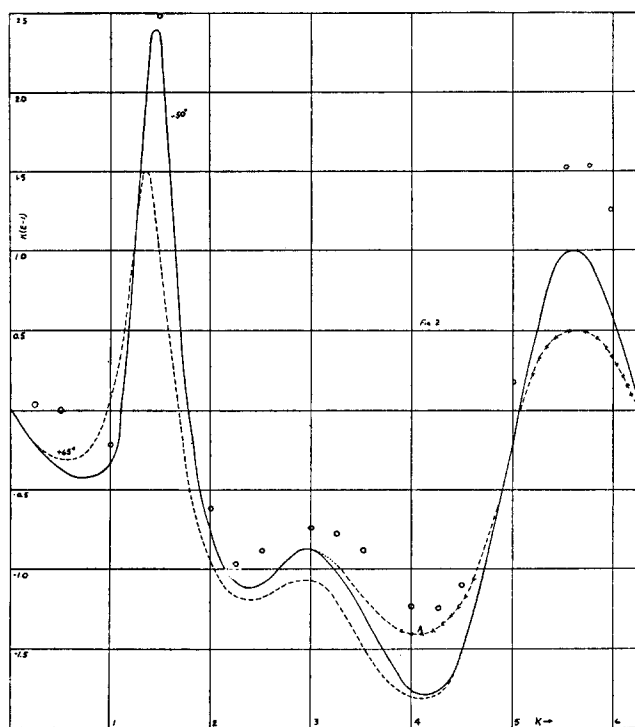


FIG. 2.  $K(E-1)$  curves for *n*-heptane ——— 50°; ..... 65°; \* \* \* \* smoothed data for -50°; o o calculated from  $q(r)$ .

molecules must be in a somewhat parallel arrangement because of their shape and size. The free space in a liquid is probably small in comparison to the volume occupied by the molecules, and there is not sufficient space for adjacent molecules to turn endwise with respect to one another. Two widely separated molecules may, however, have any orientations.

The packing of the molecules seems to be in a hexagonal arrangement for it appears from the  $q(r)$  curve that each molecule has on the average about six neighbors. This is deduced from the area under the peak, about four atoms. Since the average number of atoms at a distance of 4.5 to 6.5 Å is about twenty-five (as computed from molecular volume) the total number at this distance is about twenty-nine. This would require about six neighboring molecules.

The results of the present calculation may also be interpreted by the cybotactic theory, for if the

arrangement were crystalline the distribution function would be about the same as found. Warren and Gingrich<sup>8</sup> have applied the Fourier integral analysis to the scattering from a solid, sulfur, and obtain a distribution similar to that given by a liquid.

The question as to the validity of the use of the Fourier integral theorem was raised because the data do not extend beyond  $K = 2\pi$  while the integration must be performed in the limits  $K = 0$  to  $K = \infty$ . An attempt to find the magnitude of the probable error was made by calculating the intensity function from the  $q(r)$  curve. The portion of this from  $r = 0$  to  $r = 4\pi$  was expressed as a Fourier series by the harmonic analyzer and the integration of Eq. (1) was performed. The calculated  $K(E-1)$  curve is shown by the circles of Fig. 2 and by the upper  $E$  curve

<sup>8</sup> B. E. Warren and N. S. Gingrich, Phys. Rev. **46**, 368 (1934).

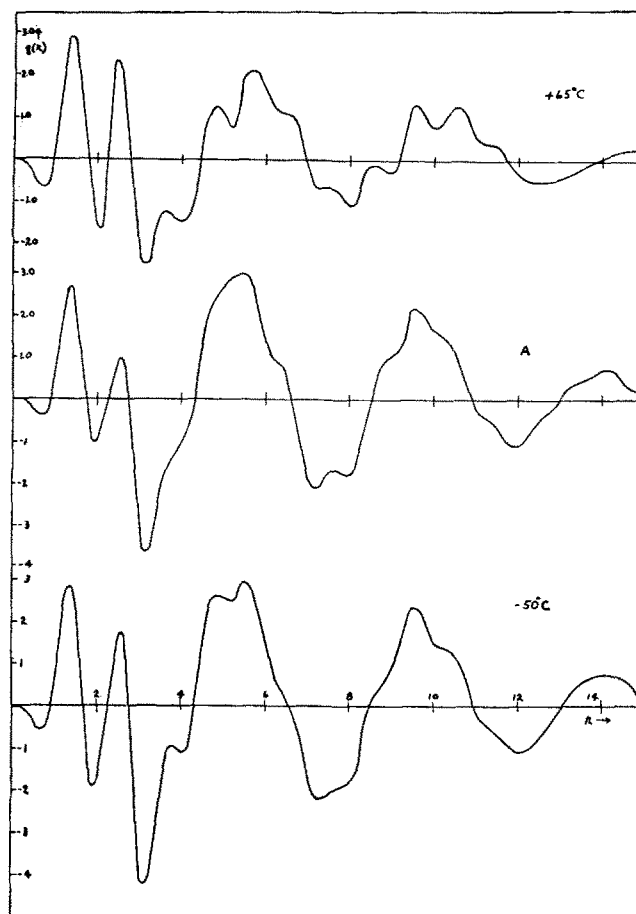


FIG. 3. Distribution function for *n*-heptane. The  $q(r)$  values give the number of atoms in excess of the average at radial distance  $r$ .

of Fig. 1. The calculated intensity is somewhat too high by a nearly constant factor but the shape of the curve is the same as the original and the peaks are at the same positions. The small fluctuations at large  $r$  values in the  $q(r)$  curve may be due to the finite integration. (Another possibility is in the extrapolation of the scattering curve to zero scattering angle.)

The success of the calculation in giving both the inner and outer structures of the liquid emphasizes the importance of the Fourier integral method of analysis and shows the need for more quantitative data extending to large angles.

The writer desires to express his thanks to Professor W. H. Zachariasen for his helpful criticisms.