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A NEUTRON DIFFRACTION STUDY OF KRYPTON
IN THE LIQUID STATE

by

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A NEUTRON DIFFRACTION STUDY OF KRYPTON IN THE LIQUID STATE

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ABSTRACT

A study was made of the neutron diffraction patterns obtained from krypton in the liquid state under seventeen conditions of temperature and pressure between 117°K and 210°K. The diffraction patterns were obtained by use of one of the neutron diffractometers of the Metallurgy Division of the Argonne National Laboratory.

Neutrons of 1.05- $\text{\AA}$ wavelength were selected from a beam of neutrons from the CP-5 reactor by reflection from the (111) planes of a single copper crystal, and this nearly monochromatic beam was incident upon the sample. The patterns obtained at 117°K, 133°K, 153°K, 183°K, and 210°K were repeated at least three times to obtain more reliable patterns for making further analysis. These diffraction patterns are the first ever reported for liquid krypton, and they show four well-defined prominences at the lower temperatures and three at the higher temperatures.

This program required the development of apparatus with unique characteristics which would permit the containment of the sample at elevated pressures. The krypton under study filled a volume of 0.660-in. diameter and 1.5-in. height in a cell fabricated from an aluminum single crystal grown especially for this research. This cell withstood pressures up to 55 atmos while contributing to the cell scattering of neutrons in an amount lower than ever reported by anyone for this kind of work. The cell was housed in an evacuated cryostat and kept at temperatures ranging from 117°K to 210°K at values constant to within 0.05°K by electronic controlling circuits, and the original charge was contained in a closed system for the duration of the experiment. After appropriately correcting the diffraction patterns for effects of background scattering, incoherent scattering, and empty cell scattering, the intensity data were Fourier transformed to give the atomic radial distribution function at each of the temperatures. The calculations were performed by use of the computer GEORGE of the Argonne National Laboratory. The speed of this computer made it feasible to investigate the sensitivity of the resultant distribution functions to arbitrary adjustment in the input data. Studies were made of the effect on the distribution of (1) terminating the calculation at arbitrary points, (2) using different values of incoherent scattering correction, (3) using different estimates of independent scattering, and (4) modifying the data by arbitrary exponential factors.

Atomic distributions at all temperatures showed nondiscrete first peaks, indicating that no molecule is formed. For the five temperatures at which the liquid was carefully studied, the positions of the first peaks and the number of nearest neighbors to which the first peak areas correspond are as follows: 117°K, 4.02 Å, 8.4 atoms; 133°K, 4.03 Å, 7.9 atoms; 153°K, 4.08 Å, 7.0 atoms; 183°K, 4.10 Å, 6.4 atoms; 210°K, 4.20 Å, 4 atoms. The number of nearest neighbors was found to be closely proportional to the density of the liquid.

By use of the series of distribution functions calculated from arbitrarily terminated data, it was shown that the width of the potential bowl of liquid krypton is in approximate quantitative agreement with that of the Lennard-Jones potential. This series of patterns also indicate that some relevant information remains unobserved beyond the range of experimental observation.

CHAPTER I

INTRODUCTION

The discovery of X rays by Roentgen¹ and the recognition by von Laue² of their wave characteristics gave scientists for the first time a powerful and direct tool with which to study the microscopic structure of matter. The distribution of atoms in any of the three forms of matter could be determined by use of this short-wavelength radiation.

The crystalline state of matter was the first to be studied by means of X rays.³ Because the static atomic lattice of long-range order characteristic of that state produced intense and easily measured diffraction effects in narrowly defined angular regions, rapid progress was made in this field. Fruitful work on liquids came somewhat later than for crystals, even though von Laue^{4,5} and his associates made observations on the scattering of X rays by liquids as early as 1912. Friedrich⁶ and Debye and Scherrer⁷ made

¹W. C. Roentgen, Sitzungsber der Wurzburger, Physik-Medic. Gesellsch. Jahrg. (1895).

²W. Friedrich, P. Knipping, and M. Laue, Ber. Bayr. AK. Wiss., 303 (1912).

³W. L. Bragg, The Crystalline State, The Macmillan Co. (1934).

⁴W. Friedrich, P. Knipping, and M. Laue, Sitzber. Bayr. AK., 315 (1912).

⁵W. Friedrich, P. Knipping, and M. Laue, Ann. Physik 41, 791 (1912).

⁶W. Friedrich, Phys. Zeits. 14, 397 (1913).

⁷P. Debye and P. Scherrer, Nachr. d. Gottingen Ges., 16 (1916).

early attempts to obtain diffraction patterns of liquids and found that the typical diffraction pattern produced by a liquid consisted of a few weak and relatively broad prominences. These diffraction effects were very weak compared to the sharp distinct peaks produced by solid materials in the crystalline state.

In the early work on X-ray diffraction studies of the liquid state, it was common practice to quote a value for $d = \lambda / (2 \sin \theta)$. This quantity was used to specify the position of the first peak in the diffraction pattern, and it was often assumed that it indicated some effective spacing in the liquid. However, since this quantity is computed from Bragg's law, which is valid only in cases of long-range order, it does not correspond to any physical attribute of a liquid. Several attempts were made to formulate a qualitative theory of liquids, and these met with moderate successes. Raman and Ramanathan⁸ worked on a theory of small-angle scattering which they ascribed to local fluctuations in density, and G. W. Stewart⁹ proposed the interesting descriptive theory in which he visualized small local groupings in which the molecules were arranged in a more or less orderly fashion similar in arrangement to the crystalline form of the material. He allowed for the interchange of molecules into and out of these groups, with the percentage of the total number of molecules of the liquid existing in these groups being different for different liquids. Stewart termed this the "cybotatic" state, and although it provided a qualitative description of an intuitive idea of the liquid state it was not sufficient to be useful in describing quantitatively the results of experiments.

Keesom and de Smedt¹⁰ made an attempt to obtain quantitative results by ascribing the diffraction effects to pairs of molecules with no interference between adjacent pairs or within the individual molecules. The failure of their theory can be attributed to the fact that it was based on a model, not of a liquid, but of a diatomic gas with a form factor of constant value. Not until Zernike and Prins¹¹ showed that the diffracted intensity could be expressed in terms of the atomic density distribution, and Debye and Menke¹² showed how to invert the process, that is, to determine experimentally the scattered intensity and from it deduce the atomic density distribution, was useful quantitative interpretation of X-ray diffraction from liquids possible. In subsequent years many liquids have been studied by X-ray diffraction and their atomic density distributions determined, with particular emphasis given to the study of elements in the liquid

⁸Raman and Ramanathan, Proc. Ind. Assn. Cult. Sci. 8, 127 (1923).

⁹G. W. Stewart, Rev. Mod. Phys. 2, 116 (1930).

¹⁰W. Keesom and J. de Smedt, Amsterdam Akad. 25, 118 (1922).

¹¹Zernike and J. Prins, Zeits. f. Physik 41, 184 (1927).

¹²P. Debye and H. Menke, Ergeb. d. Tech. Rontgenk, II, (1931).

state, since they form the simplest liquids and hence best lend themselves to theoretical study. Gingrich¹³ has summarized the results of studies which were made on 23 elements in the liquid state prior to 1943.

Experiments performed by Halban and Preiswerk¹⁴ and by Mitchell and Powers¹⁵ demonstrated the diffraction of neutrons and disclosed the possibility of a powerful new tool to be used in the study of the structure of matter. Although the radium-beryllium sources used by these experimenters gave sufficient neutron flux to allow a demonstration of the wave nature of neutrons, it was not until the advent of nuclear reactors that a neutron flux of sufficient magnitude was available for general diffraction work. As in the case of X-ray diffraction, early experimenters in neutron diffraction concerned themselves mainly with matter in the solid state. Chamberlain,¹⁶ in 1950, used neutron diffraction techniques to study liquid sulphur, lead, and bismuth, and Sharrah and Smith¹⁷ in 1953 used one of the Oak Ridge neutron diffractometers to study lead and bismuth in the liquid state at different temperatures. More recently, neutron diffraction patterns have been obtained for oxygen,¹⁸ nitrogen,¹⁸ argon,^{18,19} helium,²⁰ neon,²¹ mercury²² and for the liquid alkali metals,²³ and in each case the radial distribution of atomic densities was obtained by Fourier transform of the observed scattered intensities.

Neutron diffraction should be considered as a supplement to rather than a substitute for X-ray diffraction. Because the flux of neutrons from a nuclear reactor is much less than the photon flux from an ordinary X-ray tube, usually more time is required to obtain a neutron diffraction pattern than to obtain an X-ray diffraction pattern with comparable information.

¹³N. S. Gingrich, *Rev. Mod. Phys.* 15, 90 (1943).

¹⁴H. Halban and P. Preiswerk, *C. R. Acad. Sci. Paris.* 203, 73 (1936).

¹⁵D. P. Mitchell and P. N. Powers, *Phys. Rev.* 50, 486 (1936).

¹⁶O. Chamberlain, *Phys. Rev.* 77, 305 (1950).

¹⁷P. C. Sharrah and G. P. Smith, *J. Chem. Phys.* 21, 228 (1953).

¹⁸D. G. Henshaw, D. G. Hurst, and N. K. Pope, *Phys. Rev.* 92, 1229 (1953).

¹⁹D. G. Henshaw, *Phys. Rev.* 105, 976 (1957).

²⁰D. G. Hurst and D. G. Henshaw, *Phys. Rev.* 100, 994 (1955).

²¹D. G. Henshaw, *Phys. Rev.* 111, 1470 (1958).

²²G. H. Vineyard, *J. Chem. Phys.* 22, 1665 (1954).

²³N. S. Gingrich and LeRoy Heaton, *J. Chem. Phys.* 34, 873 (1961).

In order to compensate for the low flux, it is the practice in neutron diffraction to use large samples to increase the total number of scattered neutrons, which then requires a diffractometer of large size to yield sufficient resolution. It is indeed fortunate that the mass absorption coefficient of most materials for neutrons is quite low so that a sample of large size can generally be used to good advantage.

One of the advantages of neutron diffraction methods is that many materials which cannot be satisfactorily studied by X rays as commonly used can be studied by this means. One such material is liquid krypton. While no diffraction work has been reported for liquid krypton, there is a general interest in the atomic distributions of the noble-gas liquids, and neutron diffraction work has been reported for helium,⁽²⁰⁾ neon,⁽²¹⁾ and argon,^(18,19) and extensive X-ray work has been done on argon by Eisenstein and Gingrich,²⁴ who reported on patterns taken in the liquid, vapor, and critical regions. Since these liquids are composed of spherically symmetric atoms which are electrically neutral and do not combine to form molecules, they lend themselves well to theoretical study. Krypton is perhaps the best of the noble-gas liquids to be studied by neutron diffraction methods. Its liquid state exists in the temperature range from 103°K to 210°K, thus allowing a liquid-nitrogen-cooled cryostat to be employed, it has a high coherent scattering cross section for thermal neutrons and low incoherent and absorption cross sections, its density has been determined²⁵ over a wide range of temperatures, and it is commercially available in highly pure form.

The present work was undertaken in an attempt to obtain neutron diffraction patterns as accurately as possible for liquid krypton at selected values of temperature and pressure along the vapor pressure curve and to calculate from these the corresponding atomic radial distribution functions. Particular emphasis was placed on obtaining neutron diffraction patterns of krypton in the liquid state at the lowest possible values of temperature because the diffraction patterns and the corresponding radial distribution functions are more sharply defined near the triple point of the liquid.

²⁴A. Eisenstein and N. S. Gingrich, *Phys. Rev.* 62, 261 (1942).

²⁵C. A. Crommelin, E. Mathias, and J. J. Meihuizen, *Comp. Rendus*, 204, 630 (1937).

CHAPTER II

THEORY

The interpretation of the diffraction of neutrons by liquid samples has generally been carried out by use of the theory developed by Zernike and Prins⁽¹¹⁾ and by Debye and Menke⁽¹²⁾ for the interpretation of X-ray scattering by liquids.⁽¹⁷⁻²³⁾ Since it is not necessary in the development of this theory to make any assumptions concerning the type of radiation which is scattered by the atom or to make any assumptions about the mechanism by which the atoms scatter the radiation, there is no reason why the theory should not apply equally well to neutron scattering as to X-ray scattering. Debye's equation giving the intensity scattered by atoms of types m and n which are separated by a distance of r_{mn} is as follows⁽²⁵⁾:

$$I = \sum_m \sum_n f_m f_n (\sin s r_{mn}) / s r_{mn} \quad . \quad (1)$$

For the case of X rays, I in this equation is measured in electron units and is usually designated I_{eu} ; the quantities f_m and f_n are the atomic scattering factors for atoms m and n, respectively, and s is $(4\pi \sin \theta) / \lambda$. X rays are scattered by the electrons of the atoms, and because the radius of the atom is of the same order of magnitude as the wavelength of the X rays interference occurs between scattering from electrons in different parts of the atom. The fact that the electrons do not scatter independently makes it necessary to introduce the atomic structure factor f_i which expresses the scattering from the i^{th} atom in terms of the scattering from a free electron. The atomic structure factor is a function of the number of electrons in the atom and the scattering angle.

Neutrons are not scattered by electrons, but by atomic nuclei. The diameter of an atomic nucleus is of the order of 10^{-13} cm, which is 10^5 smaller than the neutron wavelength of 10^{-8} cm. Because the nucleus is negligibly small compared to the wavelengths of neutrons used, there is no observable interference between scattering from different parts of the nucleus. The radiation is thus scattered effectively by a point source and is isotropic for neutrons of appropriate energy or wavelength. Because of this, the atomic form factor for neutron diffraction is a constant for each element and need not be known for interpretation of diffraction patterns of elements in the liquid state.

The isotropic nature of neutron scattering allows an approximate incoherent-scattering correction to be made by subtracting a constant equal to the zero-angle scattering from the measured intensity. The ability to assume the form factor and the incoherent scattering to be constant with scattering angle is one of the major advantages enjoyed in the interpretation

of results of neutron diffraction over those of X-ray diffraction. By replacing f_m and f_n by b_m and b_n , the coherent-scattering lengths of atoms m and n , equation (1) is made applicable to neutron diffraction and is written as

$$I = \sum_m \sum_n b_m b_n (\sin sr_{mn})/sr_{mn} \quad (2)$$

For the case of monatomic liquids $b_m = b_n$, and the quantity $b_m b_n = b^2$. In carrying out the summation, one can sum over all the interatomic distances r_{mn} with respect to an origin atom and then take each atom in the scattering volume as the origin atom in turn. This latter summation is equivalent to multiplying the first summation by the total number of atoms in the array. For each atom in the array, one interatomic distance is zero, since for the case of $m = n$, $r_{mn} = 0$, and

$$\lim_{r \rightarrow 0} \left[\frac{\sin sr}{sr} \right] = 1$$

It may then be considered that, when the sum over m is performed, it is always equal to unity for the case of $m = n$, and equation (2) becomes

$$I = Nb^2 \left[1 + \sum'_n (\sin sr_{mn})/sr_{mn} \right] \quad (3)$$

The units of I in this case are the units of intensity scattered by a nucleus of cross section $\frac{1}{4}\pi$ barn, and will henceforth be referred to as I_{bu} . The symbol $\sum'$ is used to denote that the summation is restricted so as to exclude the origin atom, since its contribution is included in the first term of the bracket.

If a continuous distribution of atoms about the origin atom is assumed, an atomic density $\rho(r)$ may be defined as the atoms per unit volume at distance r from the origin. The quantity $4\pi r^2 \rho(r) dr$ would then be the number of atoms in a spherical shell of radius r and thickness dr about any atom within the liquid. This assumption allows the summation in equation (3) to be replaced by an integral and written as follows:

$$I_{bu} = Nb^2 \left[1 + \int_0^R 4\pi r^2 \rho(r) \frac{\sin sr}{sr} dr \right] \quad (4)$$

where the upper limit of the integral is the radius of the sample. If ρ_0 is now defined as the average atomic density, it is given by the equation $\rho_0 = N_0 d/A$ in units of atoms per unit volume, where N_0 is Avogadro's number, d is the density in grams per unit volume, and A is the atomic

weight expressed in grams. Let the term $Nb^2 \int_0^R 4\pi r^2 \rho_0 (\sin sr)/sr \, dr$ be added to and subtracted from the right side of equation (4), giving the result

$$I_{bu} = Nb^2 \left[1 + \int_0^R 4\pi r^2 \{ \rho(r) - \rho_0 \} \frac{\sin sr}{sr} \, dr + \int_0^R 4\pi r^2 \rho_0 \frac{\sin sr}{sr} \, dr \right] \quad (5)$$

The last term on the right side of equation (5) corresponds to the neutron scattering from a continuously uniform sample of density ρ_0 and radius R . Because of the large magnitude of R compared with the neutron wavelength, this term can be neglected at scattering angles greater than about 10^{-6} degree and can be dropped without introducing appreciable error in this kind of analysis.

If the substitution $i(s) = (I_{bu} - Nb^2)/Nb^2$ is made in equation (5) and the last term is dropped as suggested above, the equation may be written as

$$si(s) = \int_0^\infty 4\pi r [\rho(r) - \rho_0] \sin sr \, dr \quad (6)$$

with the upper limit taken to be infinity instead of R . This is possible since $[\rho(r) - \rho_0]$ approaches zero at a distance of several atomic diameters, which is very small compared to the sample dimensions. Equation (6) is now in the form to which the Fourier transform may be applied with the result that

$$4\pi r [\rho(r) - \rho_0] = \frac{2}{\pi} \int_0^\infty si(s) \sin rs \, ds \quad (7)$$

The form in which equation (7) is generally used is as follows:

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^\infty si(s) \sin rs \, ds \quad (8)$$

where the quantity $4\pi r^2 \rho(r)$ is known as the radial distribution function. Obtaining this function is the immediate goal of X-ray and neutron diffraction studies of liquids.

In equation (8) the experimentally determined intensity measurements properly corrected are contained in the $i(s)$ function, and successive evaluations of $4\pi r^2 \rho(r)$ are made for as many values of r as desired. The integrations must be performed graphically or numerically and for this work were done with the aid of the computer GEORGE of the Argonne National Laboratory.

CHAPTER III

APPARATUS AND EXPERIMENTAL PROCEDURE

In order to make a neutron diffraction study of krypton in the liquid state, it was necessary to use apparatus capable of fulfilling several rather specialized requirements. The angular distribution of scattered neutron intensities had to be measured and recorded as a function of scattering angle, and the sample had to be kept in the liquid state for periods of time as long as four weeks and controlled at known temperatures for as long as a week at a time. It was necessary to devise a sample holder which could withstand a pressure of 55 atmos without contributing complex diffraction patterns of its own, and a means had to be provided by which the sample cell could be filled and emptied without excessive loss of the sample material. Finally, a monochromatic source of well-collimated neutrons was required. The apparatus employed to meet these requirements will now be discussed.

A. Diffractionmeter

Discussion. The neutron diffractometer used in this work has been described by Heaton,²⁶ and is of the same general design as those discussed by Bacon.²⁷ Neutron diffractometers are similar in design to the more familiar X-ray single-crystal spectrometer with the major difference being in physical size. Although the flux from an experimental hole in a nuclear reactor is much greater than that available from a radium-beryllium source, the number of neutrons per sec per square cm available for diffraction remains very small compared with the photon flux available from a conventional X-ray tube. For this reason, the sample and beam dimensions are necessarily much greater in neutron diffraction work than in X-ray diffraction work. This being the case, it is necessary to make other dimensions large in order to have sufficient resolution. It is fortunate that most materials have low absorption coefficients for neutrons, so that large samples can generally be used. Since no characteristic lines of high intensity exist in the thermal neutron spectrum as in the X-ray spectrum, monochromatization of the neutron beam is always necessary.

The general arrangement of the neutron diffractometer is shown in Figure 1. A well-collimated beam of thermal neutrons emerges from the reactor and strikes a single crystal of copper from whose (111) planes is diffracted a beam of monochromatic neutrons of a wavelength determined by Bragg's law. Those neutrons not diffracted or absorbed by the crystal are absorbed in shielding which is provided for that purpose.

²⁶S. S. Sidhu and LeRoy Heaton, 13th Pittsburgh Diffraction Conference (1955).

²⁷G. W. Bacon, Neutron Diffraction, Oxford Press, (1955) pp. 7-14.

The monochromatic beam first passes through monitor counter C_1 and then strikes the sample where diffraction occurs. The angular distribution of scattered neutron intensities is measured by detector counter C_2 over a period of time required for C_1 to register a preset number of counts. This integrated quantity is recorded on the continuously moving chart of a Leeds and Northrup strip chart recorder. By requiring each counting period to be determined by the monitor counter, recorded intensity values are obtained which are independent of reactor power. A rate-meter associated with the monitor counter is a sensitive indicator of reactor power, and a switch associated with this meter automatically stops the diffractometer arm and the chart drive when that power falls below 50% of its full value. A cadmium shutter can be made to absorb the monochromatic beam during every fifth or every tenth counting period to take a background reading which is recorded on the chart.

Fig. 1
Neutron Spectrometer

Description. The collimator is 80.5 in. long, has an aperture which measures 0.75 in. horizontally by 1.5 in. vertically, and has external dimensions such that it can be fitted into an experimental hole in the face of the pile. The horizontal divergence of the beam is determined by the length of the collimator and the horizontal dimension of its aperture. For this collimator the horizontal divergence is given by $\theta = h/l = 0.75/80.5$ radian which corresponds to approximately one-half of a degree.

The monochromator consists of a $2\frac{1}{2} \times 5 \times \frac{5}{8}$ -in. single copper crystal which has been machined with its face parallel to the (111) planes. The crystal is mounted in a holder which allows the incident angle of the main beam to be changed, so that neutrons of various wavelengths can be selected.

When the diffractometer is not in use, the beam hole can be closed by a large motor-driven shutter which rotates in a vertical plane and is an integral part of the reactor shielding. During the use of the diffractometer, shielding against all but the monochromated beam is provided by the specially designed shielding associated with the diffractometer. Its purpose is to stop both fast and slow neutrons as well as gamma rays.

Figure 1 is a schematic diagram of the diffractometer and shows a section of the shielding in the plane of counter C_2 and the collimator. This shielding consists of 7 in. of a boron carbide and paraffin mixture which is surrounded by 5 in. of lead. Additional shielding is provided against the main beam by a uranium plate which has been placed in its path.

The monitor counter is a low-efficiency fission counter consisting of three parallel aluminum plates having the four inner surfaces coated by evaporation with a 0.1-mg/cm^2 layer of U^{235} . These plates are enclosed in a hermetically sealed container in which there is argon gas at a pressure of 1.5 atmos. While in operation, a potential difference of 300 volts is maintained across the plates. This counter is essentially a proportional counter which is triggered by fission fragments produced in fission capture of neutrons in the U^{235} . Pulses of lower energy are produced by the tube when it is triggered by alpha particles or gamma rays, but these are eliminated by means of a discriminator which is set to select only the pulses due to high-energy fission fragments. A plot of number of pulses vs. pulse height for this counter is shown in Figure 2 together with an indication of the discriminator setting.

Fig. 2

Pulse Height Distribution for
Fission Counter

Counter C_2 , which is mounted on the moving arm of the diffractometer, is a BF_3 proportional counter. This tube has a diameter of 2 in. and an active length of 20 in. The 2-in.-diameter permits taking full advantage of the beam height, and the 20-in. length serves to increase the efficiency of the counter, since the neutrons enter the end of the tube and have the

full length in which to produce a count. The counter tube is shielded on the side by 3 in. of boron carbide and 0.063 in. of cadmium, and the front slit is defined by cadmium. The 3 in. of boron carbide extend 6 in. to the front and rear of the tube, and 1 in. of boron carbide extends another 9 in. beyond the 3-in. shielding. The boron carbide is contained between concentric brass cylinders. With this shielding arrangement, the background count is reduced to about 50 cpm.

The drive mechanism of the diffractometer allows the specimen table to be rotated at half the angular velocity of the counter arm or it may remain stationary, as used in the present investigation, while the arm is moving. The specimen table is designed to support a load of 350 lb so that a cryostat or furnace can be mounted on it for studies in either the low- or high-temperature range.

A block diagram of the electronic controls associated with the diffractometer is shown in Figure 3. These controls can be classified in two groups: those of the detector circuit, and those of the monitor circuit.

Fig. 3. Electronic Controls of Diffractometer

The detector circuit consists of:

- (1) Counter C_2 , a 2-in.-diameter, 20-in.-long BF_3 proportional counter;
- (2) a preamplifier which is located at the BF_3 counter and serves to amplify and shape the signal from the counter an amount sufficient to overcome losses sustained in the 75 ft of cable

through which it must pass before it reaches the input of the linear amplifier;

- (3) a linear amplifier which amplifies the signal before it goes to the computer;
- (4) a computer which supplies a voltage to the recorder proportional to the number of counts received from the BF_3 counter. This unit has a scale from 2000 to 100,000 counts, corresponding to full scale on the recorder;
- (5) a Leeds and Northrup strip chart recorder.

The monitor circuit consists of the following components:

- (1) the fission counter described above;
- (2) a preamplifier which serves the same purpose for C_1 as the one mentioned above serves for C_2 ;
- (3) an amplifier which is used to amplify the signal before it goes to the rate meter. This unit also supplies 300 volts DC plate voltage to the fission counter;
- (4) a rate meter which shows at all times the flux level of incident neutrons;
- (5) a preset scaler able to scale to 10^6 counts, and which has a preset counting range of 10^4 to 10^6 ;
- (6) a shutter control which counts the number of preset counting periods and energizes the shutter solenoid every fifth or tenth period.

B. The Temperature Controller

An electronic temperature-control unit for use in this work was constructed by the Electronics Division of the Argonne National Laboratory. This unit is versatile, dependable, and capable of controlling the temperature of a sample at any value between the temperature of liquid helium and room temperature for very long periods of time with no adjustment. As shown in Figure 4a (a schematic diagram of the temperature controller) and Figure 4b (its power supply), a reference voltage, known and variable from 0 to 7 mv is obtained from a helipot which is part of a voltage divider across which is connected a mercury standard cell. This reference voltage is connected in opposition to the thermocouple output, and the voltage difference between the two sources is an input signal to the Brown Chopper Amplifier. The chopper amplifier converts the DC signal input to an AC signal, amplifies it and converts it back to DC so that the output is proportional to the input. The output from the Brown Amplifier provides an input signal to a cathode follower from which the output voltage may vary from 4.2 volts to 8 volts.

Fig. 4a. Temperature Control Unit

This voltage is applied to the base of a PNP power transistor amplifier, and together with 6 volts applied to the emitter serves as a bias voltage. The B voltage for this amplifier is provided by the DC power supply composed of T2 and the 1N1084 full-wave rectifier network. The heater coil which is wound on the heater cylinder of the sample assembly serves as the load resistor for the transistor amplifier.

Fig. 4b. Power Supply for Temperature Control Unit

The output of the Brown amplifier is a DC voltage which is greater than and proportional to the DC input voltage from the helipot and the thermocouple. A centered-scale milliammeter in series with the grid resistor of the cathode follower is a sensitive indicator of the voltage difference between the thermocouple output and the helipot output. Full scale on this meter corresponds to a potential difference of about 10 microvolts, which, in the range of interest, results from a temperature difference of about one-third of a degree centigrade. Since the scale has 25 divisions and the maximum variation of the meter pointer during operation is two divisions, it is estimated that the temperature variation of the sample is not more than $\frac{1}{30}^{\circ}\text{C}$. Under ideal conditions this unit is capable of maintaining the thermocouple temperature to a value sufficiently constant so that the pointer cannot be observed to move.

A milliammeter is in series with the heater to indicate the heater current at all times. To help prevent overshooting when the thermocouple calls for heat, several ranges of heater current have been provided. It is

generally true that use of the lowest current range with which control can be accomplished at the desired temperature will result in the least variation of temperature at the thermocouple.

C. Cryostat and Vacuum System

Since the triple point temperature of krypton is 104°K , a temperature well above the temperature of liquid nitrogen at atmospheric pressure, a cryostat using liquid nitrogen as a coolant is ideal for this experiment. The cryostat used was designed to allow the neutron-diffracting sample to be maintained at a known and adjustable temperature in the range between the temperature of liquid nitrogen and room temperature, although in this experiment it was not necessary to elevate the temperature of the sample above 210°K , which is the temperature of the critical point of liquid krypton.

Fig. 5. Cryostat

Referring now to Figure 5, the vacuum chamber is 6 in. in diameter and 30 in. high with O-ring seals at points A, B and C. The O-ring at A serves to seal the base to the vacuum chamber, and the one at B makes a vacuum seal between the upper and lower assemblies, while the one at point C serves as a sliding vacuum seal and allows the liquid nitrogen tank to be raised and lowered to adjust the sample position.

²⁸Rev. Sci. Instr. 27, 411 (1956)

The liquid nitrogen tank is made of stainless steel and is 3 in. in diameter and 10 in. deep. It is suspended by a thin-wall stainless steel tube which allows the tank to be filled but prevents excessive heat conduction to the liquid nitrogen and prevents the O-ring at point C from becoming excessively cold.

One of the thermocouple entrances is shown in Figure 5. To pass the wires through the rubber stopper, a hypodermic needle was pregreased and pushed through the stopper, the wire was threaded through the needle, and the section of the wire which was to remain in the stopper was thoroughly coated with vacuum grease, and finally the needle was removed, leaving the wire in the stopper. The stopper was coated with grease and pressed in place. This provided a very good vacuum seal.

The vacuum system used with the cryostat consists of a 4-in.-diameter oil diffusion pump and a 530-liter/min mechanical forepump, plus a cold trap and five valves. A schematic diagram of the vacuum system is shown in Figure 6. The purpose of the five-valve arrangement is to allow the cryostat to be opened and closed again without the necessity of cooling the diffusion pump. The use of silicone diffusion pump oil offers additional protection against any harmful effects which might be incurred should the diffusion pump accidentally be opened to atmospheric pressure while its oil is hot.

Fig. 6. Vacuum System

The pressure within the vacuum chamber is measured by means of a Philips gauge and a thermocouple gauge, and is continuously indicated by a meter reading directly in mm of mercury. During operation of the cryostat at low temperature, a pressure of about 10^{-6} mm of mercury was generally indicated.

D. Sample Holder

As has been previously discussed, the sample used in a neutron diffraction study must be larger in size than would be used in a comparable X-ray diffraction experiment. The large physical size of the specimen

posed several problems which had to be overcome in order to carry out the study of liquid krypton over a wide range of temperatures and pressures. These problems and how they were overcome by use of a new type of sample holder will now be discussed.

The ideal sample holder to be used in this experiment should meet the following list of requirements. It should:

- (1) yield little or no diffraction pattern of its own within the angular range to be studied,
- (2) have a low incoherent scattering cross section for thermal neutrons,
- (3) have a low absorption cross section for thermal neutrons,
- (4) have a high thermal conductivity to decrease the thermal gradient in the sample, and
- (5) have the ability to withstand high pressures so that studies near the critical point can be made.

The sample cells which have been used in the past have generally consisted of thin-walled cylinders of polycrystalline aluminum or polycrystalline vanadium. Although sample holders made from both of these materials have certain desirable features, neither of them is able to satisfy all of the above requirements.

Although vanadium has a coherent scattering cross section so low that it produces no diffraction pattern of its own, it has an incoherent scattering cross section so high that a sample cell made from it must have a very thin wall if the empty-cell correction is to be made without difficulty. This requirement prevents the satisfaction of conditions (4) and (5) above. In addition, thin vanadium was found to be brittle and crack when cooled to the temperature of liquid nitrogen.

Polycrystalline aluminum gives rise to a diffraction pattern of its own, but can be used as a sample cell provided the cell is made of very thin stock. Henshaw⁽²¹⁾ used a 0.065-in.-wall cylinder to study liquid neon and had difficulty in making the empty-cell corrections. The thin-wall requirement again prevents the satisfaction of conditions (4) and (5).

In an attempt to satisfy all of the requirements outlined above, a sample holder was made from a single crystal of aluminum. The conditions were met by the new sample holder in the following way:

- (1) The crystal could be so oriented that it produced no diffraction maxima in the regions of interest. Two very broad weak maxima did occur, as shown in Figure 7, but these caused no difficulty in making the empty-cell correction.

(2) and (3) The incoherent and absorption cross sections for aluminum are both very low. A measurement of the transmission of neutrons by the sample holder showed that 92% of the neutrons striking the sample holder were transmitted by it.

(4) and (5) Since conditions (1), (2), and (3) are well satisfied, there is no need to impose a thin-wall requirement on a single-crystal sample holder. The tensile strength of the single-crystal aluminum was determined, and a sample holder was designed to contain a pressure of 100 atmos with no yield. For a 0.660-in. internal diameter, a 0.220-in. wall thickness was required. The total thermal conductivity of aluminum together with the thick wall of this sample holder reduced the thermal gradient to $0.6^{\circ}\text{C}/\text{in.}$ during operation. Therefore, conditions (4) and (5) are well satisfied by the single-crystal sample cell.

Fig. 7. Neutron Diffraction Pattern of .22-in. Wall Single Crystal Aluminum Sample Holder

Single crystals of aluminum 7 in. long, and tapered from 1.5 in. in diameter at the top to 1 in. at the bottom, were grown by the Bridgman method and were used in the construction of two sample assemblies, shown in Figures 8 and 9. The first, built mainly for the purpose of perfecting machining, welding, and etching techniques, has a 0.100-in. wall thickness and can be used in the range of pressures up to about 20 atmos. The second, with a 0.220-in. wall thickness, was constructed for the purpose of carrying out experiments in the critical region of krypton, at which the pressure is 55 atmos. Because it was desirable to keep the thermal gradient as low as possible, and because it was considered wise to allow a margin of safety between the pressure requirements of the experiment and the designed strength of the sample holder, the second sample holder was designed to contain 100 atmos. As shown in Figures 8 and 9, the major difference in design between the two sample holders is that the high-pressure cell is provided with acme threads which serve to reduce the stress on the weld when pressure is applied.

Fig. 8. Sample Assembly #1 for Liquid Krypton

Fig. 9. High Pressure Sample Assembly for Liquid Krypton

Referring to Figure 9, it is seen that a plate at the top of the assembly is connected directly to the bottom of the liquid nitrogen tank. Separated from the plate by a rod of aluminum, 1.5 in. long, across which a thermal gradient can exist, is a 2-in.-diameter threaded aluminum cylinder on which is wound a 70-ohm heater made of doubly-silk-insulated, 7.6-ohm/ft manganin wire. A copper-constantan thermocouple is imbedded in this cylinder, which, together with the heater winding, allows the temperature to be controlled at required values above the temperature of the coolant. A $\frac{3}{32}$ -in.-diameter super-nickel tube passes through the heater cylinder and serves as a pressure line to the sample. Each sample holder has a length of 3 in. and a 0.660-in. inside diameter.

The plate which attaches to the liquid nitrogen tank, the 1.5-in. rod, and the heater cylinder were machined from a single piece of 2S aluminum using normal lathe operations. The crystal was machined by use of the lathe; precautions were taken to prevent straining and excessive heating during the machining process. The tool bits were kept very sharp and lights cuts were always taken. After machining, the crystal was etched in a bath of 30% H_2O , 34% HCl , 34% HNO_3 , and 2% HF . Since this bath produces a rather rough surface, the piece was alternately etched in a bath of 90% H_3PO_4 , 5% HNO_3 , and 5% H_2SO_4 , which tends to smooth the surface. Laue patterns were taken to insure that the polycrystalline surface produced in machining had been removed by the etching process. It was necessary to remove about 0.010 in. to eliminate all of the polycrystalline surface.

The super-nickel tube was soldered into the heater cylinder as shown in Figure 9, using a solder which is commercially available under the trade name "Inter-Act." (The solder was developed for soldering

aluminum but will also solder many other difficult-to-solder metals. It is made from an alloy of aluminum and zinc, and has a flux of sodium, lithium, and potassium which is contained in the core.) The large-crystal sample holder was then screwed tightly into the heater cylinder and heliarc welded with precautions being taken to prevent melting of the "Inter-Act" solder or excessive heating of the single crystal. The assembly was then helium checked for vacuum tightness and tested in the cryostat.

E. Crystals

The aluminum single crystals required for the construction of the sample holders were grown by means of the furnace and graphite mold shown in Figure 10. The furnace is so designed that it can be raised at a constant speed while the graphite mold and the furnace bomb remain stationary. The furnace bomb is evacuated by use of a mechanical pump to prevent oxidation of the aluminum. Aluminum from a pig of 99.99% purity was used, and in each case a piece was machined to fit the graphite mold so that the resulting crystal would be full size. Both the aluminum and the mold were thoroughly washed in acetone before placing in the furnace bomb. After the mold had been placed in the bomb and the thermocouple put in place, the bomb was evacuated and the furnace heater turned on. To insure a complete melt, the thermocouple in the graphite mold was raised to a temperature of 735°C , which is 75°C above the melting point of aluminum. When this temperature had been reached, the raising mechanism was engaged, and the furnace was raised at a rate of 2 in./hr, allowing the aluminum to cool from the bottom. A switch automatically turned off the raising mechanism and the furnace heat supply when the furnace had reached a height great enough to insure complete solidification of the aluminum.

Fig. 10
Furnace for Growing Crystals

Figure 11 shows a photograph of one of the crystals grown by this method, together with the prototype sample holder and a blank of the high purity polycrystalline aluminum.

Fig. 11. Polycrystalline Blank, Single Crystal and Sample Assembly

F. Filling System

A drawing of the system used to fill the sample holder is shown in Figure 12. The filling system was constructed of $\frac{1}{4}$ - and $\frac{3}{16}$ -in.-diameter copper tubing and six Hoke helium-tested valves. All joints were made using soft solder, including the joint to the super-nickel tube which connects to the sample holder. To fill the sample holder, the following procedure was used: with the valve on the krypton gas pressure tank closed and with V_2 , V_3 , V_4 , and V_6 open, the system was evacuated.

Fig. 12
Sample Holder Filling System

With V_3 closed and the temperature of the sample cell at about 115°K , at which temperature the vapor pressure of krypton is less than one atmosphere, the krypton gas was allowed to enter the system at a gauge pressure of 5 psi. If V_2 were closed before the sample was filled, the pressure as indicated by the dial gauge was observed to decrease; thus by opening and closing V_2 one could observe the rate of condensation of the krypton. When, on closing V_2 , no decrease in pressure was observed, the sample holder was considered to be filled. That the sample holder was full was further evidenced by the increased number of counts registered by the detector counter.

In order to reach the lowest possible temperature, it was necessary that the pressure of the sample be no greater than the vapor pressure of krypton. To insure this condition, the pressure was decreased by use of a vacuum pump to about one-half of an atmosphere and allowed to increase to equilibrium by boiling. After equilibrium had been reached, all valves were closed and the sample was contained until the series of patterns had been completed.

To remove the krypton from the sample holder at the end of a series of runs, the temperature of the sample was set at about 130°K while the pressure tank was placed in liquid nitrogen. The krypton in the pressure tank was frozen, lowering the pressure in the tank to a fraction of a millimeter of mercury. Then valves V_2 and V_6 were opened and the krypton from the sample holder passed back into the pressure tank. The pressure tank was then allowed to slowly return to room temperature.

CHAPTER IV

CORRECTIONS TO THE DATA

In order to make use of equation (8) to find the radial distribution of atomic density in the liquid being studied, it is necessary to obtain a true measure of the coherently scattered neutron intensities. Therefore, the intensity measurements must be corrected to account for scattering from the empty cell, background scattering, and incoherent scattering.

The relative ease with which neutron diffraction patterns can be corrected as compared with X-ray diffraction patterns is one of the attractive features of the neutron diffraction technique which in part compensates for the difficulties caused by the lower flux available for neutron work. As discussed earlier, the easier corrections arise in part from the essentially isotropic nature of neutron scattering which causes the scattering factor and the incoherent-scattering correction to be constant with scattering angle. Thus the correction for incoherent scattering can be made by subtracting a constant from the intensity measurements, and no form-factor normalization need be done. Another advantage enjoyed by neutron work is that no polarization correction of the intensity measurements is required.

A. Empty-cell Correction

In addition to the neutrons scattered by the liquid sample and registered by the detector-counter, other neutrons are counted which have been scattered by the sample holder, by the windows of the cryostat, and by the surrounding air. In addition to these, there is an additional background which amounts to about 50 cpm arising from imperfect shielding of this and other experiments in the reactor room. It was necessary to correct the intensity measurements for neutrons from these sources.

The approximate correction for the scattering from windows, air, and sample holder was made by obtaining an empty-cell pattern and subtracting the intensity measurements of this pattern from the total scattering pattern. Although the sample cell has a wall thickness of 0.220 in., the scattered intensity from it amounted only to about 12% of the intensity from a filled cell. Since both aluminum and krypton have a high transmission coefficient for thermal neutrons, scattering from the sample cell is considered in this work to be essentially the same when filled as when empty. Hence the correction afforded by simply subtracting the pattern taken with the cell empty should be very satisfactory. This assumption has been quite generally made by the various experimenters in the field.⁽¹⁷⁻²¹⁾ As explained in Chapter III, the amount of empty-cell correction was greatly reduced by use of a cell made from an aluminum single crystal grown especially for this experiment. The neutron diffraction pattern of the empty cell, shown in Figure 7, clearly demonstrates this fact.

B. Background-count Correction

The neutron diffractometer is provided with a cadmium shutter which can be caused to intercept the monochromatic beam during every fifth or tenth counting period during which time the background count is taken and recorded on the chart. Normally, this background remains constant for long periods of time, but on occasion, when the arrangement of neighboring experimental equipment has been changed, a difference may be noted in its magnitude. Since the background is measured and recorded at approximately one-degree intervals in scattering angle, correction for it is easily made by subtracting it from the measured intensity at the adjacent point.

C. Incoherent-scattering Correction

It has been assumed by the experimenters in this field⁽¹⁷⁻²¹⁾ that the incoherent scattering from the sample materials is approximately isotropic in nature, an assumption which allows the incoherent-scattering correction to be made by subtracting from the intensity curve (after the sample holder and background corrections have been made) a quantity, constant with angle, equal to the value of the zero-angle scattering. The value of the zero-angle scattering cannot be measured because the large number of counts recorded at the zero angle due to the main beam obscures the relatively few incoherently scattered neutrons. Therefore, the zero-angle intercept is found by extrapolating the scattering curve to zero in some reasonable way. It has been determined that the radial distribution function is relatively insensitive to the value of the incoherent scattering assumed and since the choices of the zero intercept are constrained to fall within a narrow range, no great error can be made in this correction. In practice, when a high-speed computer is available to make the Fourier transforms, several values of incoherent scattering are used and the one is accepted which produces the least spurious effect in the radial distribution functions.

D. Determination of the $i(s)$ Curve

In Chapter II, $i(s)$ was defined as $(I_{bu} - Nb^2)/Nb^2$. Since it is necessary to use this quantity in equation (8) to find the radial distribution function, it is necessary to identify the quantity Nb^2 from the experimental data. The quantity b^2 has been identified as the coherent intensity scattered by a single atom. Then if N such atoms scatter independently, that is, with no interference between the scattering from the different atoms, the total scattering is equal to Nb^2 . Because the ordering in a liquid is short range, the scattered intensity at large angles approaches the free atom scattering Nb^2 . Referring to the intensity curve in Figure 13,

$$i(s) = \frac{I_{bu} - K}{K - C} \quad ,$$

where K is equal to the independent coherent scattering plus the incoherent scattering, and C is equal to the incoherent scattering; it follows that $(K - C)$ is the independent coherent scattering.

Fig. 13. Neutron Diffraction Pattern of Liquid Krypton,
 $T = 117^{\circ}\text{K}$

E. Curve Fitting

Because it is not usually possible to determine the exact value of K to be used in this equation, two methods have been used in conjunction with each other to help in its selection. In the first method, a range of reasonable values of K is selected by visual observation of the $I(s)$ curve, and then several values K_1, K_2, K_3 , etc., within this range are chosen. The Fourier transform is then made for each case, and the resulting radial distribution showing the fewest known spurious effects is accepted as being most nearly correct. It is true in this case as it was for the incoherent scattering that the range of reasonable values is narrow, and within this range the radial distribution function is relatively insensitive to K . Because this method requires several Fourier transforms to be performed for each diffraction pattern, it would be impractical if calculations had to be performed by hand, but it is feasible if an electronic computer is available to perform the Fourier transforms.

The second method used to determine the proper value of K results from equation (8). If this equation is divided through by r^2 , it may be written as

$$4\pi\rho(r) = 4\pi\rho_0 + \frac{2}{\pi} \int_0^{\infty} s^2 i(s) \frac{\sin rs}{rs} ds \quad .$$

In the limit as r goes to zero, $(\sin rs)/rs$ approaches unity, $\rho(r)$ becomes zero, and the equation is written in the following form:

$$0 = 4\pi\rho_0 + \frac{2}{\pi} \int_0^\infty s^2 i(s) ds$$

A further rearrangement gives the equation

$$-2\pi^2\rho_0 = \int_0^\infty s^2 i(s) ds \quad (9)$$

Since in practice it is not possible to measure $i(s)$ to infinity, the upper limit of this integration must be changed from ∞ to s_m , where s_m is the maximum value of s for which $i(s)$ is measured. Beyond this point, it is assumed that $i(s) = 0$.

With this change having been made, equation (9) was used as a guide in determining the proper value of K for each diffraction pattern. The method consists of calculating and tabulating s , s^2 , $i(s)$, and $s^2 i(s)$ at intervals of $0.01 \text{ \AA}^{-1}$ for the diffraction pattern, using in the calculation of $i(s)$ a value of K which has been selected by visual observations as the best fit to the free-atom scattering. When the calculations had been completed and tabulated, a plot was made of $s^2 i(s)$ as a function of s , and the area under the curve was measured with a planimeter. The value of the integration thus obtained was used as an aid in selecting a second K value to be used in the calculation of $i(s)$ and $s^2 i(s)$. The process of plotting and integrating was repeated, and the second value of the integral thus obtained was used in conjunction with the first to make a linear interpolation between the two trial K 's to find a third, more suitable choice of the independent scattering.

The integral $\int_0^{s_m} s^2 i(s) ds$ is much more sensitive to the choice of

K than is the radial distribution function. To illustrate this, both the integral and the radial distribution function were calculated from the intensity pattern obtained for krypton at 117°K for the cases of $K = 2.92$ and $K = 2.96$. For a proper choice of K , the integral of $s^2 i(s) ds$ has the value $-2\pi^2\rho_0$ which, for the temperature of 117°K , is equal to -0.3474 . For the case in

which $K = 2.92$ was used in the calculation of $i(s)$, $\int_0^{s_m} s^2 i(s) ds$ was found

to be 0.07 , and in the case in which $K = 2.96$ was used the integral was evaluated to be -2.04 . These examples illustrate the sensitivity of this test to a change in K . Note that by changing K from 2.92 to 2.96 , the value of the integral was changed from 0.07 to -2.04 . Thus a change in K of 1.35%

changes the value of the integral by amount equal to $5.85 (2\pi^2\rho_0)$. The sensitivity is further illustrated by noting that for the case of $K = 2.92$, the total positive area was measured to be 6.02 and the total negative area was found to be 5.95, which shows that the area sought, $2\pi^2\rho_0$, is only 5.75% of the total negative area in this trial.

The rectangle in Figure 14 has an area which represents $2\pi^2\rho_0$. Figure 14 shows a plot of $s^2i(s)$ as a function of s for the diffraction pattern which was obtained for 117°K , and Figure 15 shows radial distribution functions calculated for the two cases cited above and one for the intermediate value of $K = 2.94$; the K value of 2.93 is the one for which

$\int_0^{s_m} s^2i(s) ds$ is nearly equal to $-2\pi^2\rho_0$. It is seen from this that the radial distribution function is much less sensitive to the choice of K than is $\int_0^{s_m} s^2i(s) ds$ and that a choice of K which will make the value of this integral zero or slightly negative should provide a satisfactory fit of the scattering curve to the independent scattering. It is worth noting that in every case the choice of K by visual observation was a reasonably satisfactory value to be used in the calculation of the radial distribution function when compared to the fitting obtained by application of the criterion given in equation (9). Figure 14 demonstrates in a rather exaggerated way that there probably are some interferences beyond the limit of experimental observation presented here.

Fig. 14. $S^2 i(S)$ vs. S for Liquid Krypton, $T = 117^\circ\text{K}$
 $P = 0.8$ Atmospheres

An approach which has been used by Thompson²⁹ as an aid in fitting his experimentally measured intensities to the independent scattering curve is based on a method derived by Krogh-Moe.³⁰ It consists of essentially

²⁹C. W. Thompson, PhD Thesis, University of Missouri (1959).

³⁰J. Krogh-Moe, Acta. Cryst. 2, 951 (1956).

fitting over the entire experimental curve. The derivation of the equations used in this method was based on scattering by electronic charge. Krogh-Moe states that, although a similar derivation based on scattering centers could be made, its convergence would be slower and hence it would be less useful. The derivation would have to be based on scattering centers in order to be applicable to neutron diffraction work. For that reason, no attempt to use Krogh-Moe's method was made.

Fig. 15. Radial Distributions of Liquid Krypton for Three Different Values of Independent Scattering, $T = 117^{\circ}\text{K}$, $P = 0.8$ Atmospheres

The fully corrected $i(s)$ curve for $T = 117^{\circ}\text{K}$ is shown in Figure 16. Points 1, 2, 3, 4, 5, 6, 7 and 8 show the places at which the computation was terminated arbitrarily in an effort to determine the sensitivity of the radial distribution function to different values of K defined by these termination points. The radial distribution functions resulting in each case are shown in Figure 29 (p.). In the last case it can be seen by inspection that the $s^2i(s)$ curve would be almost totally negative, yet no great change has resulted in the radial distribution function.

Fig. 16. Corrected Intensity vs. $(\sin \theta)/\lambda$ for Liquid Krypton at $T = 117^\circ\text{K}$, $P = 0.8$ Atmospheres

F. Target-nucleus-recoil Correction

The assumption of the isotropic nature of neutron scattering which is generally made, strictly speaking, holds true only in the center-of-mass coordinate systems. Because the recoil of the target nucleus is very small for heavy atoms, the center-of-mass and the laboratory coordinate systems nearly coincide for these elements, and little if any correction need be made. However, a correction of this type must be made for the light atoms, and has been necessary in the study of helium,⁽²⁰⁾ lithium,⁽²²⁾ and sodium.⁽²²⁾

The intensity scattered by the sample is proportional to the scattering cross section σ , and the counter at any time registers a counting rate proportional to an element $\delta\sigma$ of the total scattering cross section, while the counter slit occupies an element of solid angle $\delta\Omega$. The counting rate, then, is proportional to $\delta\sigma/\delta\Omega$. Since $\delta\Omega$ is very small, $\delta\sigma/\delta\Omega$ may reasonably be approximated by $d\sigma/d\Omega$.

Because the total scattering into the counter slit is independent of the reference frame, $\delta\sigma_L = \delta\sigma_C$ where $\delta\sigma_L$ is an element of the scattering cross section in the laboratory coordinate system, and $\delta\sigma_C$ is the corresponding element in the center-of-mass system. However, the element of solid angle occupied by the counter slit is a function of the reference frame in which it is expressed. Therefore, the relationship between $d\sigma_L/d\Omega_L$ and $d\sigma_C/d\Omega_C$ is given by

$$d\sigma_L/d\Omega_L = (d\sigma_C/d\Omega_C)(d\Omega_C/d\Omega_L) \quad .$$

Ringo³¹ has given $d\Omega_c/d\Omega_L$ as follows:

$$\frac{d\Omega_c}{d\Omega_L} = \frac{\left[1 + \frac{2M_n}{M_t} \cos \theta_c + \left(\frac{M_n}{M_t}\right)^2\right]^{3/2}}{1 + \frac{M_n}{M_t} \cos \theta_c}$$

When this substitution is made for $d\Omega_c/d\Omega_L$, the relationship obtained is as follows:

$$\frac{d\sigma_L}{d\Omega_L} = \frac{d\sigma_c}{d\Omega_c} \frac{\left[1 + \frac{2M_n}{M_t} \cos \theta_c + \left(\frac{M_n}{M_t}\right)^2\right]^{3/2}}{1 + \frac{M_n}{M_t} \cos \theta_c} = f(\theta) \frac{d\sigma_c}{d\Omega_c}$$

The relation between θ_L and θ_c is given by the equation³¹

$$\tan \theta_L = \frac{\sin \theta_c}{\frac{M}{M_t} + \cos \theta_c},$$

where θ_L is the scattering angle in the laboratory coordinate system.

In practice, $f(\theta)$ is calculated for as many values of θ as is necessary to plot the corrected intensity curve accurately. Each $I(\theta_i)$ is multiplied by the quantity $f(\theta)/f(\theta_i)$. The correction increases with increasing θ to a maximum at 180° . In the present experimental arrangement, the maximum scattering angle is about 100° , for which the correction factors for helium, lithium, sodium, and krypton would be 1.78, 1.38, 1.17, and 1.02, respectively. It is seen here that the maximum correction for the krypton case is negligibly small.

In this correction, the assumption is made that the recoil of the target nucleus is the same as if it were free. This is perhaps not a strictly valid assumption, but for the cases of lithium and sodium it proved to be satisfactory. It is not known if this is the exact form of correction used in the liquid helium work, but it is assumed that it was generally similar.

³¹G. R. Ringo, Handbuch der Physik, Springer-Verlag, XXXII, pp. 552.

CHAPTER V

RESULTS

The radial distribution of atomic densities of krypton in the liquid state, the immediate aim of this experiment, was determined by use of equation (8) after the intensity measurements had first been corrected as described in Chapter IV. The radial distribution function $4\pi r^2 \rho(r)$ has the units atoms per angstrom, and when multiplied by an element of radius dr , gives the number of atomic scattering centers between r and $r+dr$, where r is the distance from the center of any atom in the liquid sample. It follows, then, that the number of atoms between any two distances r_1 and r_2 can be determined by integration of this function between the limits r_1 and r_2 . Such an integration gives the number of atoms in a spherical shell of inner radius r_1 and outer radius r_2 . As has been discussed by Vineyard,³² the radial distribution function does not contain enough information to allow the determination of the three-dimensional configuration of atoms in the liquid, but it does give the atomic density as a function of r , from which the number of nearest neighbors, the nearest-neighbor distance, and often the number of second nearest neighbors and their distances can be determined. It is sometimes possible to use this information in conjunction with other considerations to make reasonable deductions concerning the actual configuration of atoms in the liquid. No such deductions are attempted in this study; rather, it is limited to finding the radial distribution functions at a number of selected temperatures and pressures, and from each of them, to calculate the number of nearest neighbors and nearest-neighbor distance.

The relationship of the radial distribution function $4\pi r^2 \rho(r)$ to the corrected coherent intensity $i(s)$ is given by equation (8) in the form

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^{S_m} s i(s) (\sin rs) ds \quad .$$

The term $4\pi r^2 \rho_0$ can easily be calculated for any value of r by simple multiplication, so that the problem really consists of evaluating the integral. Since s and $i(s)$ cannot be evaluated for infinitely large values of s , the integration must be terminated at some $s = s_m$ which is the largest value for s for which $i(s)$ can be measured, and the assumption is made that $i(s)$ is zero for all values of s greater than s_m . The necessity of terminating the intensity measurements at finite $s = s_m$ can introduce some error in the radial distribution function, but it is shown in Chapter VI that the integrated area of the first peak of the distribution functions remains nearly constant when the integral is terminated at various values of s beyond the third prominence in $I(s)$.

³²G. H. Vineyard, Liquid Metals and Solidification, (Am. Soc. for Metals, Cleveland, 1958) pp. 51-53.

To determine the value of the function $4\pi r^2 \rho(r)$ at one value of r , it is necessary to evaluate the integral $2r/\pi \int_0^S s i(s) (\sin rs) ds$ and add the result to the quantity $4\pi r^2 \rho_0$. To determine the entire radial distribution function, it is necessary to perform the operation for as many values of r as may be required to plot the curve of $4\pi r^2 \rho(r)$. For example, if the radial distribution function were to be determined in the range from zero to $10 \text{ \AA}$ at intervals in r of $0.2 \text{ \AA}$, it would be necessary to evaluate the integral fifty times. One technique that has been commonly used consists of plotting the function $s i(s) \sin rs$ for each value of r and then of measuring the area under the curve by use of a planimeter. Since in the example cited above it would be necessary to do this complete operation fifty times for each pattern, it is evident that this method is extremely tedious.

A second method which has been employed is a method of trigonometric interpolation.³³ It depends on expressing the $s i(s)$ curve in an approximate analytic form; a finite trigonometric series is chosen in such a way that the integral for each of a chosen set of values of r becomes simply related to one of the coefficients of the series. It is also possible to make use of a harmonic analyzer in performing the integrations.

When available, a high-speed electronic computer can be used to eliminate much of the labor of evaluating the integral, and allow calculation of the radial distribution function for many conditions of termination, free-atom scattering, and incoherent scattering, a process which would be impractical because of length under conditions of manual integration. The computer GEORGE of the Argonne National Laboratory was used to good advantage in this work.

The experimental intensity curves were corrected for background and sample-holder scattering as explained in Chapter IV, and the result was plotted as a function of $(\sin \theta)/\lambda$, and the corrected intensity values were read from the plot at intervals of $0.001 \text{ \AA}^{-1}$. This information along with the value of the zero-angle intercept C , the free-atom scattering K , and the density of the sample ρ_0 at the temperature at which the intensity measurements were made was then given to the Applied Mathematics Division of the Argonne National Laboratory where the information was supplied to the computer by means of a punched tape. Each intensity point was labeled with an integral number j , in the range $0 \leq j \leq n$, where n is the total number of intensity measurements. For each data point the computer changed the value of $(\sin \theta)/\lambda$ to the appropriate value of s by multiplying by 4π , converted the intensity measurements to $i(s)$ by forming the quotient $(I - K)/(K - C)$, and then formed the product $(j\Delta s)i(j\Delta s)\sin(rj\Delta s)$ and summed all of the values of the products. The sum was then multiplied

³³ P. C. Sharrah, Ph.D. Thesis, University of Missouri (1942).

by the factor $2 r \Delta s / \pi$ and the result added to $4 \pi r^2 \rho_0$. The result was then punched on the tape along with the corresponding value of r , and the computer increased the value of r by $0.2 \text{ \AA}$, and the computation began again. The total process was fully automatic once the computation had been started, and no further information had to be furnished the computer. When the computer had finished the total computation, the output tape was passed through a decoding machine which typed out the value of the radial distribution function at intervals of $0.2 \text{ \AA}$ in r between zero and $25 \text{ \AA}$.

A typical $si(s)$ curve is shown in Figure 17. It was plotted from the intensity data which are tabulated in Table I for liquid krypton at 117°K . The plot makes it clear that the small prominences at large angles in the intensity curve are quite important in the integral. Although the isotropic nature of neutron scattering reduces the sensitivity of the integral to the high-angle neutron intensity prominences compared with the sensitivity of the integral to comparable prominences in an X-ray diffraction pattern, they remain highly significant, and their intensities must be measured as carefully as possible. To improve experimental precision, at least three complete diffraction patterns were taken under identical conditions of temperature and pressure at each of the five conditions of temperature and pressure for which liquid krypton was studied, and the averaged curves were the ones used for subsequent analysis.

Fig. 17. $Si(S)$ vs S for Liquid Krypton
 $T = 117^\circ\text{K}$, $P = 0.8$ Atmospheres

Table I

CORRECTED INTENSITY OF NEUTRON PATTERNS OF KRYPTON

$(\sin \theta)/\lambda \text{ (\AA}^{-1}\text{)}$	T	117°K	T	133°K	T	153°K	T	183°K	T	210°K	$(\sin \theta)/\lambda \text{ (\AA}^{-1}\text{)}$	T	117°K	T	133°K	T	153°K	T	183°K	T	210°K
0.000	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.305	2.70	2.70	2.70	2.70	2.70	2.70	2.70	2.70	2.70	2.70
0.005	0.01	0.02	0.01	0.02	0.04	0.06	0.09	0.15	0.22	0.305	0.310	2.56	2.56	2.61	2.61	2.61	2.61	2.61	2.61	2.61	2.61
0.010	0.02	0.04	0.02	0.03	0.05	0.07	0.09	0.15	0.22	0.310	0.315	2.43	2.44	2.52	2.52	2.52	2.52	2.52	2.52	2.52	2.52
0.015	0.03	0.05	0.03	0.05	0.07	0.09	0.15	0.22	0.310	0.320	0.320	2.31	2.32	2.42	2.42	2.42	2.42	2.42	2.42	2.42	2.42
0.025	0.05	0.10	0.06	0.09	0.15	0.22	0.310	0.320	0.320	0.325	0.325	2.20	2.22	2.31	2.31	2.31	2.31	2.31	2.31	2.31	2.31
0.030	0.06	0.12	0.08	0.11	0.18	0.27	0.36	0.45	0.54	0.330	0.330	2.11	2.12	2.21	2.21	2.21	2.21	2.21	2.21	2.21	2.21
0.035	0.07	0.13	0.11	0.14	0.22	0.31	0.40	0.50	0.60	0.335	0.335	2.04	2.05	2.16	2.16	2.16	2.16	2.16	2.16	2.16	2.16
0.040	0.08	0.15	0.13	0.17	0.25	0.34	0.43	0.53	0.63	0.340	0.340	2.00	2.01	2.12	2.12	2.12	2.12	2.12	2.12	2.12	2.12
0.045	0.09	0.16	0.16	0.19	0.29	0.38	0.48	0.58	0.68	0.345	0.345	1.99	2.00	2.12	2.12	2.12	2.12	2.12	2.12	2.12	2.12
0.050	0.10	0.18	0.18	0.23	0.33	0.42	0.52	0.62	0.72	0.350	0.350	2.02	2.03	2.15	2.15	2.15	2.15	2.15	2.15	2.15	2.15
0.055	0.10	0.19	0.21	0.26	0.38	0.47	0.57	0.67	0.77	0.355	0.355	2.07	2.07	2.20	2.20	2.20	2.20	2.20	2.20	2.20	2.20
0.060	0.11	0.21	0.25	0.29	0.42	0.51	0.61	0.71	0.81	0.360	0.360	2.13	2.14	2.26	2.26	2.26	2.26	2.26	2.26	2.26	2.26
0.065	0.12	0.23	0.27	0.33	0.47	0.56	0.66	0.76	0.86	0.365	0.365	2.21	2.22	2.34	2.34	2.34	2.34	2.34	2.34	2.34	2.34
0.070	0.14	0.25	0.32	0.38	0.52	0.61	0.71	0.81	0.91	0.370	0.370	2.30	2.31	2.42	2.42	2.42	2.42	2.42	2.42	2.42	2.42
0.075	0.16	0.26	0.36	0.43	0.58	0.67	0.77	0.87	0.97	0.375	0.375	2.39	2.41	2.49	2.49	2.49	2.49	2.49	2.49	2.49	2.49
0.080	0.18	0.30	0.40	0.48	0.65	0.74	0.84	0.94	1.04	0.380	0.380	2.49	2.52	2.56	2.56	2.56	2.56	2.56	2.56	2.56	2.56
0.085	0.20	0.35	0.45	0.55	0.73	0.82	0.92	1.02	1.12	0.385	0.385	2.57	2.61	2.63	2.63	2.63	2.63	2.63	2.63	2.63	2.63
0.090	0.23	0.43	0.51	0.64	0.84	0.93	1.03	1.13	1.23	0.390	0.390	2.65	2.67	2.69	2.69	2.69	2.69	2.69	2.69	2.69	2.69
0.095	0.27	0.53	0.58	0.75	0.98	1.07	1.17	1.27	1.37	0.395	0.395	2.72	2.70	2.73	2.73	2.73	2.73	2.73	2.73	2.73	2.73
0.100	0.36	0.67	0.67	0.90	1.15	1.24	1.34	1.44	1.54	0.400	0.400	2.77	2.72	2.75	2.75	2.75	2.75	2.75	2.75	2.75	2.75
0.105	0.46	0.82	0.77	1.10	1.34	1.43	1.53	1.63	1.73	0.405	0.405	2.79	2.72	2.76	2.76	2.76	2.76	2.76	2.76	2.76	2.76
0.110	0.61	1.13	0.98	1.37	1.59	1.68	1.78	1.88	1.98	0.410	0.410	2.79	2.71	2.76	2.76	2.76	2.76	2.76	2.76	2.76	2.76
0.115	0.85	1.42	1.26	1.73	1.88	1.97	2.07	2.17	2.27	0.415	0.415	2.76	2.70	2.76	2.76	2.76	2.76	2.76	2.76	2.76	2.76
0.120	1.20	1.79	1.64	2.15	2.17	2.26	2.36	2.46	2.56	0.420	0.420	2.72	2.67	2.74	2.74	2.74	2.74	2.74	2.74	2.74	2.74
0.125	1.75	2.33	2.17	2.64	2.43	2.52	2.62	2.72	2.82	0.425	0.425	2.66	2.63	2.71	2.71	2.71	2.71	2.71	2.71	2.71	2.71
0.130	2.47	3.02	2.77	3.13	2.74	2.83	2.93	3.03	3.13	0.430	0.430	2.62	2.60	2.69	2.69	2.69	2.69	2.69	2.69	2.69	2.69
0.135	3.60	3.95	3.49	3.62	3.00	3.09	3.19	3.29	3.39	0.435	0.435	2.57	2.57	2.65	2.65	2.65	2.65	2.65	2.65	2.65	2.65
0.140	4.87	4.88	4.21	3.86	3.07	3.16	3.26	3.36	3.46	0.440	0.440	2.53	2.54	2.62	2.62	2.62	2.62	2.62	2.62	2.62	2.62
0.145	5.73	5.43	4.63	3.81	3.06	3.15	3.25	3.35	3.45	0.445	0.445	2.48	2.52	2.59	2.59	2.59	2.59	2.59	2.59	2.59	2.59
0.150	5.77	5.36	4.66	3.55	2.97	3.06	3.16	3.26	3.36	0.450	0.450	2.45	2.50	2.56	2.56	2.56	2.56	2.56	2.56	2.56	2.56
0.155	5.20	4.85	4.46	3.22	2.68	2.77	2.87	2.97	3.07	0.455	0.455	2.42	2.48	2.53	2.53	2.53	2.53	2.53	2.53	2.53	2.53
0.160	4.33	4.18	4.04	2.94	2.45	2.54	2.64	2.74	2.84	0.460	0.460	2.39	2.46	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
0.165	3.48	3.52	3.45	2.71	2.27	2.36	2.46	2.56	2.66	0.465	0.465	2.37	2.45	2.49	2.49	2.49	2.49	2.49	2.49	2.49	2.49
0.170	2.73	2.84	2.95	2.47	2.11	2.20	2.30	2.40	2.50	0.470	0.470	2.36	2.44	2.47	2.47	2.47	2.47	2.47	2.47	2.47	2.47
0.175	2.28	2.39	2.60	2.24	1.98	2.07	2.17	2.27	2.37	0.475	0.475	2.36	2.44	2.47	2.47	2.47	2.47	2.47	2.47	2.47	2.47
0.180	1.97	2.13	2.35	2.05	1.88	1.97	2.07	2.17	2.27	0.480	0.480	2.37	2.44	2.46	2.46	2.46	2.46	2.46	2.46	2.46	2.46
0.185	1.78	1.97	2.16	1.93	1.80	1.89	1.99	2.09	2.19	0.485	0.485	2.39	2.45	2.45	2.45	2.45	2.45	2.45	2.45	2.45	2.45
0.190	1.65	1.86	2.02	1.83	1.74	1.83	1.93	2.03	2.13	0.490	0.490	2.42	2.45	2.45	2.45	2.45	2.45	2.45	2.45	2.45	2.45
0.195	1.58	1.78	1.92	1.78	1.68	1.77	1.87	1.97	2.07	0.495	0.495	2.46	2.47	2.45	2.45	2.45	2.45	2.45	2.45	2.45	2.45
0.200	1.52	1.73	1.85	1.73	1.68	1.77	1.87	1.97	2.07	0.500	0.500	2.50	2.51	2.46	2.46	2.46	2.46	2.46	2.46	2.46	2.46
0.205	1.50	1.71	1.80	1.73	1.68	1.77	1.87	1.97	2.07	0.505	0.505	2.54	2.55	2.47	2.47	2.47	2.47	2.47	2.47	2.47	2.47
0.210	1.51	1.72	1.78	1.73	1.70	1.79	1.89	1.99	2.09	0.510	0.510	2.58	2.59	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
0.215	1.55	1.76	1.79	1.73	1.74	1.83	1.93	2.03	2.13	0.515	0.515	2.62	2.63	2.53	2.53	2.53	2.53	2.53	2.53	2.53	2.53
0.220	1.63	1.83	1.83	1.81	1.78	1.87	1.97	2.07	2.17	0.520	0.520	2.66	2.67	2.56	2.56	2.56	2.56	2.56	2.56	2.56	2.56
0.225	1.76	1.94	1.88	1.84	1.84	1.93	2.03	2.13	2.23	0.525	0.525	2.67	2.68	2.59	2.59	2.59	2.59	2.59	2.59	2.59	2.59
0.230	1.88	2.06	1.97	1.93	1.91	2.00	2.10	2.20	2.30	0.530	0.530	2.68	2.69	2.60	2.60	2.60	2.60	2.60	2.60	2.60	2.60
0.235	2.02	2.21	2.08	1.98	1.98	2.07	2.17	2.27	2.37	0.535	0.535	2.60	2.67	2.59	2.59	2.59	2.59	2.59	2.59	2.59	2.59
0.240	2.23	2.36	2.19	2.11	2.04	2.13	2.23	2.33	2.43	0.540	0.540	2.66	2.67	2.56	2.56	2.56	2.56	2.56	2.56	2.56	2.56
0.245	2.44	2.55	2.31	2.20	2.11	2.20	2.30	2.40	2.50	0.545	0.545	2.64	2.65	2.53	2.53	2.53	2.53	2.53	2.53	2.53	2.53
0.250	2.65	2.74	2.43	2.29	2.18	2.27	2.37	2.47	2.57	0.550	0.550	2.62	2.63	2.51	2.51	2.51	2.51	2.51	2.51	2.51	2.51
0.255	2.85	2.90	2.57	2.38	2.25	2.34	2.44	2.54	2.64	0.555	0.555	2.60	2.61	2.49	2.49	2.49	2.49	2.49	2.49	2.49	2.49
0.260	3.03	3.04	2.72	2.47	2.31	2.40	2.50	2.60	2.70	0.560	0.560	2.57	2.58	2.45	2.45	2.45	2.45	2.45	2.45	2.45	2.45
0.265	3.15	3.15	2.86	2.56	2.35	2.44	2.54	2.64	2.74	0.565	0.565	2.54	2.55	2.44	2.44	2.44	2.44	2.44	2.44	2.44	2.44
0.270	3.18	3.19	2.95	2.64	2.38	2.47	2.57	2.67	2.77	0.570	0.570	2.52	2.53	2.44	2.44	2.44	2.44	2.44	2.44	2.44	2.44
0.275	3.20	3.20	2.99	2.70	2.39	2.48	2.58	2.68	2.78	0.575	0.575	2.51	2.52	2.44	2.44	2.44	2.44	2.44	2.44	2.44	2.44
0.280	3.18	3.19	2.99	2.71	2.37	2.46	2.56	2.66	2.76	0.580	0.580	2.51	2.52	2.44	2.44	2.44	2.44	2.44	2.44	2.44	2.44
0.285	3.14	3.14	2.97	2.69	2.34	2.43	2.53	2.63	2.73	0.585	0.585	2.51	2.52	2.44	2.44	2.44	2.44	2.44	2.44	2.44	2.44
0.290	3.05	3.06	2.93	2.62	2.31	2.40	2.50	2.60	2.70	0.590	0.590	2.51	2.52	2.44	2.44	2.44	2.44	2.44	2.44	2.44	2.44
0.295	2.95	2.96	2.86	2.55	2.26	2.35	2.45	2.55</

Fig. 18
Density of Liquid Krypton as
a Function of Temperature

Fig. 19
Neutron Diffraction Pat-
terns of Liquid Krypton
($\lambda = 1.05 \text{ \AA}$)

Table II
DENSITY OF LIQUID KRYPTON AT DIFFERENT TEMPERATURES
(Reference 25)

Temp °K	Density gm/cm ³	Density atoms/Å ³	Temp °K	Density gm/cm ³	Density atoms/Å ³
208.20	1.1926	0.0086	170.92	1.9674	0.0142
205.99	1.3171	0.0095	163.68	2.0350	0.0146
201.90	1.4590	0.0105	153.33	2.1363	0.0154
199.63	1.5161	0.0109	144.03	2.2202	0.0160
193.59	1.6379	0.0118	134.12	2.3048	0.0166
188.38	1.7255	0.0124	125.96	2.3707	0.0171
180.82	1.8338	0.0132			

The average density ρ_0 as determined from this plot is 0.0176 atoms/ $\text{\AA}^3$ at 117°K, and this value was used in the calculation of the radial distribution function. The radial distribution function thus obtained is shown in Figure 20. The most important features of the curve consist of two major concentrations of atoms at 4.02 and 7.8 $\text{\AA}$ with a value of approximately zero between zero and 3.3 $\text{\AA}$. The first major peak, which represents the number of nearest neighbors, is not discrete, a feature which shows that no molecule is formed, and has an area corresponding to 8.5 atoms. The second major peak is not well enough resolved to allow a reasonably unique determination of its area.

Fig. 20. Radial Distribution of Liquid Krypton
T = 117°K, P = 0.8 Atmospheres

Closer inspection of the radial distribution function reveals small ripples in the region between zero and 3.3 $\text{\AA}$. In this region there should be no indication of matter, and the ripples can only be described as being spurious. The ripples are quite small, and they represent a net area corresponding to one-fiftieth of an atom.

The radial distribution function shows a small peak at $r = 5 \text{ \AA}$. The reality of such a concentration of atoms existing between the first and second nearest-neighbor groups is open to serious question. Because of the existence of the small ripples in the region between zero and 3.3 $\text{\AA}$, the possibility exists that the peak at 5 $\text{\AA}$ is a similar spurious effect resulting from the same cause. The most likely causes of such a spurious effect are improper choices of the incoherent scattering or the free-atom scattering, or it could be caused by the necessity of terminating the integral in equation (8) at the finite value $s = s_m$. These three possibilities were investigated in some detail, and that investigation will be discussed in Chapter 6.

In the same manner as that just discussed, neutron diffraction patterns of liquid krypton at temperatures of 117°K, 133°K, 153°K, 183°K and 210°K (see Figure 19) were obtained, corrected, and transformed to give the radial distribution functions. The fully corrected intensities are listed in Table I as functions of $(\sin \theta)/\lambda$ at intervals of $0.005 \text{ \AA}^{-1}$. This is a sufficient number of intensity points to allow accurate plots of the intensity curves to be made, from which intermediate values can be obtained should they be needed.

The correct intensities are plotted in Figure 19 for each of the temperatures. The horizontal dashed line in each curve in Figure 19 is the value of the independent scattering obtained in each case, as described in Chapter IV.

Several changes are observed to take place in the diffraction pattern as the temperature is increased. The main diffraction peak shifts slightly to the left with increased temperature. It moves from a $(\sin \theta)/\lambda$ value of $0.148 \text{ \AA}^{-1}$ at 117°K to $(\sin \theta)/\lambda = 0.141 \text{ \AA}^{-1}$ at 210°K. This change is not large but is consistent with observations of Eisenstein and Gingrich for argon.

A change, wrought by temperature, which is much more pronounced than the shift of diffraction prominences, is the change in intensity of those prominences. The intensity of each peak decreases as the temperature is increased until the fourth peak ultimately disappears at 183°K. The first peak decreases by a substantial amount with each increase in temperature and becomes broader. This is graphically depicted in Figure 21, which shows the first peak of each of the diffraction patterns. It can be seen that the maximum intensity falls from about 5,800 neutrons/min at 117°K to 3,000 neutrons/min at 210°K.

Fig. 21. First Peak of Diffraction Patterns at Different Temperatures

The diffraction maxima are all smooth, with no fine structure superimposed on any of the major prominences.

The intensity measurements as recorded in Table I were used to calculate the radial distributions at each of the five temperatures. Results of these calculations are recorded in Table III at intervals in r of 0.2 Å, and the distribution functions are plotted in Figure 22.

Several interesting observations can be made from this series of curves. First, the number of atoms in the first coordination sphere decreased continuously with increasing temperature. If the area is measured in such a way as to exclude the subsidiary peak, the number of nearest neighbors is found to decrease from 8.4 at 117°K to 4 at 210°K. If the area is measured so as to include the subsidiary peak, the area decreases from 12 atoms at 117°K to 7.2 atoms at 210°K.

Table III

RADIAL DISTRIBUTION FUNCTION FOR LIQUID KRYPTON

Radius (Å)	T 117°K	T 133°K	T 153°K	T 183°K	T 210°K	Radius (Å)	T 117°K	T 133°K	T 153°K	T 183°K	T 210°K
0.00	0.000	0.000	0.000	0.000	0.000	10.00	21.946	21.043	19.180	15.725	8.797
0.20	0.006	0.021	0.003	0.024	0.001	10.20	23.682	22.451	20.260	16.516	9.292
0.40	0.028	-0.052	-0.010	-0.066	-0.022	10.40	25.698	23.751	21.436	17.356	9.694
0.60	-0.113	0.028	-0.039	-0.091	0.086	10.60	26.392	24.996	22.514	18.242	10.026
0.80	-0.101	0.080	0.100	0.116	-0.168	10.80	27.510	26.111	23.444	19.150	10.423
1.00	0.053	0.190	-0.121	0.147	-0.202	11.00	28.560	26.917	24.308	20.054	10.959
1.20	0.120	0.147	-0.008	-0.108	0.150	11.20	29.438	27.459	25.161	20.934	11.688
1.40	-0.067	-0.085	0.154	0.068	0.061	11.40	30.048	28.030	25.968	21.766	12.355
1.60	-0.261	0.303	0.134	0.269	0.037	11.60	30.446	28.758	26.637	22.511	12.835
1.80	0.120	0.245	-0.115	0.256	0.123	11.80	30.788	29.436	27.117	23.151	13.104
2.00	0.230	0.073	0.303	0.031	-0.244	12.00	31.196	29.920	27.527	23.743	13.279
2.20	0.367	0.354	0.152	0.308	0.272	12.20	31.767	30.442	28.136	24.384	13.516
2.40	0.237	0.385	0.201	-0.238	-0.184	12.40	32.582	31.309	29.099	25.128	13.883
2.60	0.171	0.242	0.345	0.104	0.121	12.60	33.641	32.485	30.260	25.935	14.340
2.80	0.164	0.010	0.088	0.250	-0.261	12.80	34.851	33.719	31.373	26.719	14.800
3.00	0.185	-0.354	-0.287	-0.423	0.584	13.00	36.159	34.953	32.441	27.452	15.224
3.20	0.608	-0.529	0.168	0.297	0.764	13.20	37.649	36.334	33.644	28.178	15.637
3.40	0.286	0.472	1.061	0.341	-0.353	13.40	39.395	37.868	34.967	28.960	16.091
3.60	3.434	3.337	3.520	2.168	0.833	13.60	41.259	39.366	36.170	29.818	16.610
3.80	7.724	7.039	6.335	4.437	2.456	13.80	42.976	40.722	37.176	30.743	17.175
4.00	10.165	9.208	7.911	5.936	3.793	14.00	44.423	42.018	38.213	31.737	17.765
4.20	9.314	8.510	7.299	6.046	4.217	14.20	45.699	43.318	39.440	32.815	18.374
4.40	6.634	6.179	5.328	5.177	3.656	14.40	46.215	44.543	40.674	33.955	19.009
4.60	4.747	4.551	3.855	4.219	2.651	14.60	48.068	45.616	41.692	35.058	19.653
4.80	4.560	4.426	3.775	3.731	1.945	14.80	49.087	46.592	42.603	36.137	20.258
5.00	4.911	4.734	4.309	3.704	1.936	15.00	50.051	47.574	43.673	37.089	20.787
5.20	4.667	4.557	4.430	3.918	2.428	15.20	51.081	48.624	44.904	38.000	21.249
5.40	4.138	4.328	4.254	4.253	2.873	15.40	52.189	49.794	46.060	38.937	21.706
5.60	4.179	4.694	4.484	4.633	2.867	15.60	53.326	51.109	47.082	39.918	22.215
5.80	4.830	5.298	5.083	4.886	2.476	15.80	54.527	52.489	48.176	40.910	22.779
6.00	5.537	5.527	5.429	4.883	2.130	16.00	55.890	53.788	49.464	41.879	23.342
6.20	6.243	5.785	5.586	4.794	2.222	16.20	57.398	54.992	50.807	42.832	23.845
6.40	7.445	6.982	6.395	5.032	2.784	16.40	58.912	56.265	52.071	43.808	24.297
6.60	9.234	9.006	8.106	5.855	3.509	16.60	60.388	57.743	53.348	44.830	24.773
6.80	10.995	10.724	9.811	7.078	4.060	16.80	61.975	59.374	54.763	45.889	25.362
7.00	12.254	11.544	10.688	8.257	4.360	17.00	63.797	61.016	56.239	46.904	26.087
7.20	13.279	12.136	11.117	9.129	4.606	17.20	65.739	62.605	57.616	48.063	26.884
7.40	14.506	13.230	11.931	9.778	5.031	17.40	67.555	64.146	58.905	49.224	27.658
7.60	15.744	14.508	13.050	10.394	5.658	17.60	69.156	65.648	60.238	50.470	28.357
7.80	16.384	15.172	13.672	10.990	6.282	17.80	70.662	67.142	61.643	51.767	28.999
8.00	16.246	15.010	13.579	11.429	6.674	18.00	72.184	68.681	63.015	53.049	29.644
8.20	15.786	14.838	13.434	11.674	6.787	18.20	73.694	70.250	64.313	54.280	30.328
8.40	15.484	14.753	13.708	11.881	6.784	18.40	75.138	71.760	65.629	55.492	31.031
8.60	15.389	14.772	14.068	12.225	6.868	18.60	76.570	73.195	67.049	56.732	31.706
8.80	15.379	14.868	14.120	12.703	7.105	18.80	78.077	74.666	68.569	57.992	32.327
9.00	15.538	15.244	14.177	13.175	7.396	19.00	79.651	76.236	70.138	59.211	32.916
9.20	16.921	16.012	14.816	13.556	7.623	19.20	81.226	77.801	71.707	60.351	33.520
9.40	17.115	17.044	16.028	13.916	7.775	19.40	82.821	79.281	73.211	61.467	34.171
9.60	18.507	18.230	17.279	14.381	7.969	19.60	84.529	80.795	74.615	62.649	34.866
9.80	20.155	19.583	18.265	14.997	8.314	19.80	86.372	82.487	75.991	63.930	35.579
						20.00	88.253	84.272	77.470	65.245	36.298

Fig. 22. Atomic Distributions of Liquid Krypton

Figure 23 shows a plot of the first peak, excluding the subsidiary peak, of each of the radial distributions. It clearly illustrates the decrease in the total area and the decrease in the first maximum of the distribution function as the temperature is increased. The first intensity peak position, average density, number of atoms in the first coordination sphere, and the radius of the first coordination sphere for each temperature are given in Table IV.

This work was subject to the following experimental limitations:

(1) Temperature Measurement. The temperature of the sample was measured by use of two Bureau of Standards calibrated copper-constantan thermocouples, of $\pm 0.1^\circ\text{K}$ guaranteed accuracy, in conjunction with a Leeds and Northrup K-2 potentiometer. During the experiment, the temperature of each thermocouple is believed to have been known to a precision of $\pm 0.2^\circ\text{K}$. However, as discussed in Chapter III, a thermal gradient of $0.6^\circ\text{K}/\text{in.}$ existed in the sample, causing a temperature difference of 0.9°K across the 1.5 in. of krypton which was the diffracting portion of the sample, and of 1.8°K across the entire 3-in. length of the sample. Hence, while the mean temperature of the sample is known to a precision of approximately $\pm 0.2^\circ\text{K}$,

it would be proper to assign limits of precision of $\pm 0.6^\circ\text{K}$ when speaking of the temperature of the neutron diffracting sample.

Fig. 23. First Peak of Radial Distribution Function at Different Temperatures

Table IV
SOME PARAMETERS OF LIQUID KRYPTON

Temperature, °K	Pressure, atmos	Density, atoms/Å ³	First Intensity Peak (sin θ)/ λ	Nearest Neighbor Distance Å	Number of Nearest Neighbors
117	0.8	0.0176	0.148	4.02	8.4
133	2.6	0.0166	0.147	4.04	7.9
153	7.0	0.0154	0.146	4.08	7.0
183	24.2	0.0130	0.143	4.10	6.4
210	54.0	0.0075	0.141	4.20	4.0

(2) Pressure Determination. Because it was not considered wise to risk contamination of the sample with the fluid of a hydraulic pressure gauge, sample pressure was not measured except at 117°K, at which temperature it was measured by means of a dial gauge. Since, at 117°K, steps were taken to insure that equilibrium existed between the liquid and vapor states, it was assumed that the remaining temperature-pressure points were near the vapor pressure curve from which the pressure could be determined.

(3) Lowest Temperature. It is desirable to obtain diffraction patterns near the triple point of a material because diffraction patterns and the corresponding radial distribution functions of the liquid state are more sharply defined in that region. Although the triple point of krypton is 104°K, it was not possible to maintain the sample in the liquid state at temperatures below 117°K. This was likely due to the fact that the temperature difference across the 3 in. of krypton was about 1.8°K, whereas the temperature difference between boiling and freezing at a mean temperature of 117°K is only 3°K. Any attempt to lower the temperature of the sample below 117°K resulted in the formation of crystals in the sample, as indicated by the diffraction pattern.

(4) Small-angle Limit. It was not possible to obtain accurate intensity measurements at values of less than 3.5° because of interference from the main beam. The intensity curves were extrapolated to zero angle in what seemed to be a reasonable way in order to determine the scattered intensity at angles less than 3.5°. This small-angle limit prevented the detection of any existing small-angle scattering.

CHAPTER VI

DISCUSSION OF RESULTS

The most important feature of the radial distribution function of liquid krypton at any of the temperatures for which it was calculated consists of the two major concentrations of atoms at roughly 4 and 7.8 Å. In addition to these, there exists in all of the distributions small spurious ripples in the region between zero and 3.3 Å, a subsidiary peak, and what appears to be a low-amplitude, high-frequency ripple superimposed on all of the primary curve.

Because of the presence of the subsidiary peak, there exists some question as to how the area which corresponds to the number of nearest neighbors should be measured. If the area of the first peak is measured as shown by the shaded portion in Figure 20, it is found to correspond to 8.5 atoms. However, if the area is measured in such a way as to include the subsidiary peak as shown by the dashed line, it is found to correspond to 12 atoms, which is in agreement with the first coordination number for the solid state of krypton. In his study of liquid sulphur, Tompson⁽²⁹⁾ found it necessary to include the area of the spurious ripples in the region of both sides of the main peak in order to obtain the correct value for the first coordination number. The net area of the spurious ripple between zero and 3.3 Å in this study corresponds to about 0.02 atom, which is an insignificant amount compared to the minimum error generally assumed in the study of liquid structure.

The number of nearest neighbors, 8.5 atoms, obtained by integration of the main peak alone is in close agreement with the 8.8 atoms found by Henshaw for neon and the 8.2 to 8.5 atoms which he found for argon. In both studies neutron diffraction techniques were used. The number 10.2 to 10.8 atoms obtained by Eisenstein and Gingrich for argon in the liquid state at 84.4°K, a temperature which is very near its triple point, by use of X rays is somewhat lower but in reasonable agreement with the 12 atoms found in this study by including the large peak as well as the small one in the integration.

When the temperatures at which the patterns were taken relative to the triple point temperatures of the materials are considered, it appears that the radial distribution of krypton at 117°K should be compared to the distributions reported by Eisenstein and Gingrich for argon at 91.8°K. Although the density had changed by only 2.6% between 84.4°K and 91.8°K, the shape of the distribution was greatly changed. Indicated in that distribution is a small subsidiary concentration of atoms between the first and second nearest-neighbor groups which is in the same position relative to the major peaks as the subsidiary peak observed for krypton in the present study. They reported an area for the first major peak ranging from

6.8 to 7.2 atoms and for the subsidiary peak an area representing 3.2 to 4.7 atoms. It follows that the total area would correspond to a quantity ranging from 10 to 11.9 atoms. This is in good agreement with the 10.2 to 10.8 which they reported for the distribution of the material at 84.4°K, and in reasonably good agreement with the 12 atoms obtained for krypton when the subsidiary peak is included in the measurement.

One of the most interesting features of the series of distributions obtained for liquid krypton is the manner in which the first peak decreases with temperature in both area and maximum height. The decrease in area of the main peak excluding the subsidiary peak as a function of temperature is in relatively good agreement with the change in average atomic density ρ_0 with increased temperature. The relationship between the first peak area and average density is shown in Figure 24. To make this plot, the quotients $\rho_0(T)/\rho_0(117)$ and $N(T)/N(117)$ were formed, where $\rho_0(T)$ is the average density at each of the five temperatures, $\rho_0(117)$ is the average density at 117°K, $N(T)$ is the coordination number represented by the area of the main peak for each temperature excluding the subsidiary peak, and $N(117)$ is the coordination number represented by the area of the main peak for 117°K. The quotients were then plotted against temperature. These plots are seen to be quite similar, indicating that the number of nearest neighbors changes in roughly the same manner as the average density.

Fig. 24. Density and Coordination Number Change as a Function of Temperature

Another feature which should be noted is that the first peak in the radial distribution function moves to the right with temperature increase. The amount of change in its position is small here, just as was the change of the position of the main diffraction maxima in the intensity pattern. However, the shift in the radial distribution may not be a totally real

effect. As discussed later in this chapter, radial distributions were calculated from arbitrarily terminated intensity data, and in these it was noted that the first peak in the radial distribution moved to higher r values as the intensity data were curtailed. The intensity data for the higher temperature cases were curtailed as a result of the pattern having become too weak to allow measurement of intensity fluctuations beyond the third peak. Hence, the shift may be the result of the inability to measure as much of the pattern at high temperature as could be measured at low temperature. A comparison of the distribution functions given by the curtailed data with the high-temperature distribution function indicates that the peak position in the distribution of krypton from the 210°K data is about the same as the peak position in distribution e in Figure 29 (see p. 52) from the terminated data. Curve e results from the transform of $2\frac{1}{2}$ peaks in $i(s)$, and the 210°K distribution results from the transform of 3 weaker $i(s)$ peaks; hence the data in these cases are roughly comparable. Although some shift in the position of the peak is expected because the average position of an atom in an asymmetric potential bowl changes if the thermal energy is changed, it appears that part of the shift in position of the first peak in the distributions of krypton at higher temperature must be regarded as being caused by abbreviation of the $i(s)$ function.

The radial distribution function for krypton at the critical point as determined in this study is more sharply defined than was observed for argon in the X-ray study by Eisenstein and Gingrich. A possible explanation is that the scattering process for X rays scattered by argon includes greater effective amplitudes of atomic motions than does the process for neutrons scattered by krypton nuclei. Since the radial distribution function represents a time average of the distribution of scattering centers, a greater range of motion would tend to smear out the distribution peaks. X rays are scattered by atomic electrons, whereas neutrons are scattered by atomic nuclei. The distribution function for argon is a distribution of centers of electronic charge of the argon atoms, and the distribution function for krypton is, in this case, a distribution of atomic nuclei. Because the interatomic forces act mainly on the electrons and these are transmitted, so to speak, to the nucleus by the forces between nucleus and electrons, and because of the relatively large mass of the nucleus compared to the electrons, it seems possible that the amplitude of motion of the center of electronic charge might be somewhat greater than the corresponding amplitude of nuclear motion. Such a situation would lend to the observation of sharper distribution functions obtained from neutron diffraction than would be observed from X-ray diffraction. A similar phenomenon is observed in the study of crystalline materials in the solid state. It has been found that the Debye factor used in the analysis of neutron diffraction patterns must be different from the one used in analysis of X-ray diffraction patterns from the same material.³⁴ This could be attributed to the amplitude of vibration of the center of electronic charge of the atoms in

³⁴M. H. Mueller, Private Communication.

the crystalline lattice being different from the amplitude of vibration of the nuclei of the atoms. If such an effect is observed in the crystalline state, it would be expected to be much greater near the critical point of the material, at which the thermal energy is very great compared to that of the material in solid state.

Because ripples known to be spurious appear in the region between zero and $3.3 \text{ \AA}$, and because the existence of a subsidiary concentration of atoms between the first and second nearest-neighbor groups is open to serious question, a careful investigation of the various sources of error which could lead to the production of a spurious result of this type was made. These investigations and their results will now be discussed.

As discussed in Chapter IV, it is not possible to measure the zero-angle scattering because it is obscured by the main beam, and its magnitude has to be determined by extrapolating the intensity pattern to zero in some reasonable way. The value thus determined is assumed to be the incoherent scattering and is subtracted from the total scattering curve. Since a possibility of error exists in choice of the zero-angle scattering, it is desirable to determine the sensitivity of the radial distribution function to such errors.

In Figure 25, the neutron diffraction pattern obtained at 117°K , point C appears to be the most reasonable choice of the zero-angle scattering, but it is possible that the proper choice could lie anywhere in the range between A and B. To determine the sensitivity of the radial distribution function to the choice of the zero-angle scattering $I(0^\circ)$, a Fourier transformation of the intensity data was performed for the cases $I(0^\circ) = A$, $I(0^\circ) = B$, and $I(0^\circ) = C$.

Fig. 25. Scattered Neutron Intensity vs $(\sin \theta)/\lambda$ for Different Values of Incoherent and Independent Scattering

The resulting radial distributions are shown in Figure 26. For case A the coordination number is 8.3, for case B it is 8.9, while case C gives 8.5. The difference between the coordination number resulting for case A and that resulting for case B is 0.6 atom, which is small compared to the total coordination number in either case. This indicates that the coordination number is relatively insensitive to the choice of $I(0^\circ)$ within the range used in this test. It can also be seen that the radial distribution function between the first and second nearest-neighbor peaks remains essentially unchanged, indicating that the peak at 5 Å is insensitive to the choice of $I(0^\circ)$ within reasonable limits.

Fig. 26. Radial Distributions for Different $I(0^\circ)$ Values
Liquid Krypton $T = 117^\circ\text{K}$ $P = 0.8$ Atmospheres

A second quantity which cannot be determined precisely is the value of the free-atom scattering. Since this term, too, is determined between narrow limits, it is a simple matter to choose several values of K in the reasonable range and perform the Fourier transform. The way this was done in practice was to terminate the integration of $\sin(s)r$ for various values of s , choosing the value of $I(s_m)$ as K . The computer then used the same input information except for the value of K and the number of intensity points; that is, the computations were stopped at points, 1, 2, 3, 4, 5, 6, 7, and 8 in Figure 25 and the value of $I(s_m)$ was used as K . The results of this series of transformations are shown in Figure 27. It is noted that the shape of the distribution curve is slightly changed when K is changed, but that in general the shape remains the same for each case. The spurious ripples in the region between zero to 3.5 Å are somewhat affected, but in no case do they become large enough to be significant compared with the main peak. The portion of the curve between 5 and 8 Å appeared to be somewhat smoother for $K = 2.92$, but the subsidiary

peak, itself, was not noticeably changed. It is also worthwhile to note that $K = 2.93$ is the value for which $\int_0^{s_m} s^2 i(s) ds$ is approximately equal to $-2\pi^2 \rho_0$.

Fig. 27

Radial Distributions for Different
Assumed Values of Independent
Scattering Liquid Krypton $T = 117^\circ\text{K}$
 $P = 0.8$ Atmospheres

The effect on the shape of the radial distribution caused by the necessity of terminating the integration of $s i(s) \sin(rs)$ at a finite value s_m is discussed by Klug and Alexander.³⁵ Such a termination causes the main peaks to be flanked by a series of ripples, the first maximum of which is located at a distance of $r = 8\pi/3s_m$ on each side of the main peak. For a termination at $s_m = 7.33 \text{ \AA}^{-1}$, ripple maxima would be expected at a distance of 1.15 Å on each side of the main peak, which corresponds to r values of 2.87 and 5.17 Å, while the radial distribution for krypton at 117°K shows the small maxima at 2.73 and 5.01 Å. Although these flanking peaks are not similar in size and shape and are not in positions symmetric with respect to the center of the main peak or in the positions predicted by the simple theory, their existence near the predicted positions casts further doubt on the validity of the subsidiary peak, and indicates that termination of the integration may be at least partially responsible for its existence.

A further investigation of the effect of a finite termination was made by purposely terminating the integration at every point for which $s i(s) = 0$. The arrows of Figure 28 show the position of these finite terminations of the integral. The radial distribution functions calculated for each case are shown in Figure 29, and the first coordination number measured for each distribution is given in Table V.

³⁵X-ray Diffraction Procedures, John Wiley & Sons, (1954) p. 608.

Fig. 28. Intensity vs $(\sin \theta)/\lambda$ Liquid Krypton $T = 117^\circ\text{K}$
 $P = 0.8$ Atmospheres Showing Arbitrary
 Terminations

Fig. 29. Radial Distributions from Terminated Data
 Liquid Krypton $T = 117^\circ\text{K}$
 $P = 0.8$ Atmospheres

Table V
COORDINATION NUMBERS RESULTING
FROM TERMINATED DATA

Distribution	Coordination Number
b	12.25
c	11.6
d	10.9
e	9.5
f	9.5
g	9.5
h	8.4

It is interesting to note how little information is required to yield the general structure of the liquid. If only the first negative portion is taken, the resulting function shows some structure about the parabola $4\pi r^2 \rho_0$. However, if the integration includes the first negative and first positive portions, the general shape of the radial distribution function is revealed. It is true that the peaks are broad and the positions are not in exact agreement with that given by using all of the intensity curve, but the agreement seems remarkable for so little information having been transformed. From point b forward, the effect of additional peaks is to add sharpness and detail to the radial distribution function. Note that by point f the small subsidiary peak clearly appears at 5.2 Å. Addition of the last part of the pattern contributes little to the shape of the radial distribution function other than a little sharpness. Although the subsidiary peak does not clearly appear before curve f, its effect can be seen as early as curve d. As can be seen in this set of curves, there are deviations from symmetry in both positions and area of the small peaks which flank the main peak, and there are deviations from their calculated positions. Although these deviations seem to support the possible reality of the subsidiary peak, the positional trend is near enough in accord with that which is expected on the basis of termination that its validity remains in doubt. It is possible that the peak may result from a combination of termination error and small errors in intensity measurements.

A fourth possibility of error is in incorrect measurement of the intensities. Because precise intensity measurements are much more easily made at the lower values of s than at the higher values, it follows that mistakes are more likely to be made in the latter part of the curve. It is

also true that any error made in the latter portion of the pattern is emphasized in the integral because it is multiplied by s which increases as θ becomes larger. The standard procedure recommended by Klug and Alexander for suppressing the ripples in the radial distribution function due to various sources of error is to apply to the $i(s)$ function a modifying factor of the form $e^{-Asin^2\theta}$. They suggest that A in this factor be chosen in such a way that at $s = s_m$ the exponential be equal to 0.1. This modifying factor is sometimes called an artificial temperature factor because of its similarity in form to the Debye temperature factor. However, its use has no theoretical justification other than to aid in the use of the experimental intensity in the $si(s)$ function more nearly in accord with the certainty of the data. It is an empirical device which has been found useful in suppressing ripples in the radial distribution function which are known to be spurious. It is sometimes suggested that a slight modifying factor may tend to suppress the spurious more than it does the real portions of the radial distribution function.

The modifying factor suggested above was applied to the $i(s)$ function of the data obtained at 117°K. It is true that it almost eliminated all effects in the distribution function which were suspected of being spurious, but, as well, it eliminated a great deal of that which would not seem to be spurious. This can be seen in Figure 30, in which the distribution function resulting from the modified data is compared to the one from unmodified data.

Fig. 30. Radial Distributions from Modified and Unmodified Data
Liquid Krypton $T = 117^\circ\text{K}$ $P = 0.8$ Atmospheres

The result of using the modifying factor is very similar to the result of terminating the integration at a lower value of s . This fact is illustrated by Figure 31 in which the radial distribution function obtained from the modified data is compared with the distribution obtained by curtailing the integration after the first two peaks. In some ways the latter distribution function is preferable. For example, the first peak has a greater height in the distribution calculated from the terminated data than in that calculated from the modified data. The valley between the first and second nearest-neighbor groups is deeper and the peak indicating the second nearest-neighbor group is better defined in the distribution which results from the terminated data. It must be pointed out, however, that the spurious ripple in the region between zero and 3.3 Å was almost completely suppressed by use of the modifying factor. It seems likely that a modifying factor as severe as the one which was used here may wash out any information regarding the fine structure of the liquid state if such were revealed by the experimental data. Hence, use of such a device carries with it the danger that real effects may be lost as well as spurious ones.

Fig. 31. Radial Distributions from Modified and Terminated Data.

In an effort to gain more information about the effect of an exponential modifying factor on the subsidiary ripples of the radial distribution function, several modifying factors of the type described above were applied to the $i(s)$ function of the intensity data obtained at 117°K. The values of the modifying functions at $s = s_m$ in these four additional cases were 0.8, 0.6, 0.4, and 0.2. The reconstructed intensity curves corresponding to the modified $i(s)$ functions are shown in Figure 32, and the resulting radial distributions are shown in Figure 33.

Fig. 32. Unmodified and Modified Intensity Functions
Liquid Krypton $T = 117^\circ\text{K}$ $P = 0.8$ Atmospheres

Fig. 33. Radial Distributions from Modified Data
Liquid Krypton $T = 117^\circ\text{K}$
 $P = 0.8$ Atmospheres

It is interesting to note in Figure 33 that only the severest modification was sufficient to completely suppress the subsidiary peak.

Perhaps the most interesting feature of the series of radial distributions is the reaction of the subsidiary peak to a change in temperature. It moves out with increased temperature and, while the area of the main peak decreases markedly with temperature increase, the area of the subsidiary peak remains of essentially constant value. Perhaps the strongest argument in favor of the reality of the subsidiary peak lies in its reaction to a temperature increase. If the information contained in the neutron diffraction pattern is limited either by termination of the intensity data or by the application of a modifying factor, the subsidiary peak either vanishes or diminishes, depending on the severity of the modification or termination; however, when the information was limited by an increase in temperature which suppressed all of the prominences of the diffraction pattern and ultimately eliminated the fourth peak, the subsidiary peak in the radial distribution function was neither eliminated nor depressed.

Fluctuations in the radial distribution similar to the peak at $r = 5 \text{ \AA}$ have been reported in several of the X-ray and neutron studies of the liquid elements. Several elements for which such fluctuations have been reported are lead, bismuth, argon, lithium, cesium, tin, indium, and cadmium. A brief survey of the literature indicates that a subsidiary peak has tended to appear only in those cases for which the diffraction pattern was strong enough to show at least three and often four strong prominences. Eisenstein and Gingrich reported such an irregularity in the argon radial distribution pattern at 91.8°K , 126.7°K , and 144.1°K . Although the effect did not appear in their work at 84.4°K , the function was not smooth in the region between the first and second coordination groups, and the area of the first peak was great enough to have included the small concentration of atoms if one in reality did exist at the higher temperature.

The results of these investigations do not establish the origin of the subsidiary peak. While some of the evidence seems to indicate that the peak is a real effect, other evidence points toward termination as being its cause. A summary of the results of the investigation is as follows: (1) A change in the fit to the free-atom scattering as well as a change in the estimate of the magnitude of the incoherent scattering left the radial distribution curve in general, and the subsidiary peak in particular, unaffected. (2) The subsidiary peak position does not coincide exactly with the position predicted for a spurious peak caused by termination error, but it is close enough to the predicted position that termination cannot be eliminated as a contributing factor. (3) If it were caused by termination error, simple theory based on an isolated concentration of atoms would predict a matching peak in a symmetric position on the left of the main peak, but the spurious ripple which does exist on the left does not match the subsidiary peak in area, is not in a position symmetric to its position,

and is not in the position predicted for a termination peak. However, in the series of curves from terminated data the general trend of the shift in position of the small peaks on either side of the main peak is similar to that predicted for termination peaks. (4) Such a peak appears in the distributions reported by many investigators for monatomic liquids. These usually result in distributions from strong diffraction patterns of 3 to 4 prominences. The general strength of their diffraction patterns supports the accuracy of their intensity measurements. (5) Eisenstein and Gingrich reported such a peak in the distributions for argon at temperatures of 91.8°K, 126.7°K, and 144.1°K. Although no such peak was found by them at 84.4°K, the area of the main peak is great enough in that distribution to include the subsidiary concentration of atoms. It looks as if the subsidiary peak moved into and became a part of the main peak as the temperature was lowered to the vicinity of the triple point. Thus it appears from this and other experiments that the subsidiary peak may have some claim to legitimacy, but in spite of a careful investigation of the possible sources of error in this work, its origin could not be firmly established and must be left as uncertain, although termination appears to be a contributing factor. Observations which appear to support its reality are its reaction to change in temperature and its failure to fulfill accurately the predictions for termination error peak, and the frequent appearance of such a peak in other similar studies, but these are not sufficiently strong arguments to establish it as corresponding to any real attribute of the liquid state. Hence, its origin, whether real or spurious, remains uncertain.

The interatomic potential function is one of the basic properties of the liquid state of which some information is given by the radial distribution function. Detailed information as to the form of the potential cannot be obtained directly, but an indication of the width of the potential bowl is given in an approximate way by the radial distribution function.

In his study of liquid argon, Henshaw took the ratio of the greatest value of r where $4\pi r^2 \rho(r)$ is zero to the value of r where $4\pi r^2 \rho(r)$ is a maximum in the first peak, and found this ratio to be 0.79. From this he concluded that the bowl of the effective potential in liquid argon is wider than that of the Lennard-Jones 12:6 potential.

The Lennard-Jones 12:6 potential, often assumed to approximate the potential function between pairs of atoms within a noble gas liquid such as krypton,³⁶ is of the form

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

³⁶G. H. A. Cole, Am. J. Phys. 27, 136 (1959).

A plot of this potential is shown in Figure 34. If this potential were assumed to exist in the liquid, the point of nearest approach of one atom to another would be represented approximately by point A, the first point in r for which $V = 0$, and the position of the nearest neighbor atom would be roughly at $r = B$, the minimum point in the potential. The ratio of A to B for this potential is 0.891. Since the nearest approach distance of nearest-neighbor atoms and the nearest-neighbor distance are given in the radial distribution function by the r value for which $4\pi r^2 \rho(r)$ is last equal to zero and by the r position of the first maximum in $4\pi r^2 \rho(r)$, respectively, such a distribution can be used to give information concerning the width of the potential bowl. However, because of thermal motion of atoms in the liquid state it should not be assumed that points A and B correspond exactly to the r values of the last density zero and the first density maximum. Any increased thermal motion would cause the density maximum to move toward larger r than that of the potential minimum, because of the asymmetry of the potential bowl, and it would also cause a shift in the density zero position to the left, although this latter shift could be expected to be small because of the strength of the repulsive force.

Fig. 34. Plot of Lennard-Jones 12:6 Potential

Observation of the series of distributions resulting from terminated data shows that both the nearest approach distance $r(0)$ and the nearest neighbor distance $r(\max)$ are dependent on the amount of the $i(s)$ curve transformed. The ratio of $r(0)$ to $r(\max)$ for each curve is given in Table VI.

Table VI

r(0) AND r(max) FOR DISTRIBUTIONS
FROM TERMINATED DATA

Distribution	s_m	$r(0),$ Å	$r(max),$ Å	$r(0)/r(max)$
b	0.170	2.62	4.46	0.590
c	0.246	3.00	4.30	0.697
d	0.310	3.12	4.20	0.742
e	0.378	3.28	4.14	0.792
f	0.440	3.30	4.08	0.809
g	0.304	3.34	4.05	0.824
h	0.580	3.38	4.02	0.841

It is seen from this table that the ratio continuously increases as more data is transformed to give the radial distribution function. It must be concluded that the correct value of the width of the potential bowl could be determined with reasonable accuracy from a radial distribution function only if the total $i(s)$ function could be measured. Since in practice it is not possible to measure the $i(s)$ function to large values of s , the ratio $r(0)/r(max)$ obtained from the distribution function must be recognized as indicating the maximum width of the potential bowl, with the actual width being somewhat less than the ratio indicates.

In the present study, the ratio $r(0)/r(max)$ obtained from the radial distribution function for krypton at 117°K is 0.84. This value is somewhat higher than the value quoted by Henshaw for argon, but it is still lower than that predicted by the Lennard-Jones potential. If the ratio is measured from radial distribution e of Figure 30, which was obtained from approximately equivalent data to the diffraction patterns reported by Henshaw from which he obtained the radial distribution function for argon, a ratio of 0.79 is obtained, in agreement with the value he quoted.

Since it is not possible to measure $i(s)$ to infinitely large values of s , an alternative procedure was tried in an effort to gain knowledge of the approximate maximum value of the ratio which could be obtained if $i(s)$ could be obtained for infinite values of s . The ratio $r(0)/r(max)$ was plotted against s_m using as points the values of $r(0)/r(max)$ and s_m obtained from the terminated data. The resulting curve, shown in Figure 35, appears to be asymptotically approaching some maximum value.

Fig. 35. $r(0)/r(\text{max})$ vs $[(\sin \theta)/\lambda]_{\text{max}}$
for Arbitrary Terminations
of $i(\text{S})$ Liquid Krypton

By performing what appears to be reasonable extrapolations, as shown by the dashed lines, this maximum value apparently lies between 0.875 and 0.91. Allowing for possible error in this type of analysis, either value is in approximate agreement with the 0.891 obtained in this approximate way from the Lennard-Jones 12:6 potential.

The evidence obtained from this series of curves does not support the conclusion of Henshaw based on determination of rather limited extent for argon, but, instead, indicates that the Lennard-Jones 12:6 potential gives a value for $r(0)/r(\text{max})$ which is well within the range of the maximum value that could be obtained for that ratio provided intensity measurements could be carried out to sufficiently large values of $(\sin \theta)/\lambda$.

CHAPTER VII

SUMMARY

The present experimental investigation was undertaken to obtain neutron diffraction patterns from liquid krypton and from them to calculate the corresponding functions that represent the distributions of krypton atoms about any given atom in the liquid. Because this chemically inert monatomic material is composed of spherically symmetric atoms for which theoretical work appears promising, diffraction studies of liquid krypton have long been recognized as being particularly attractive. However, no such work has been done because until recently X rays have been the only appropriate radiation of suitable wavelength for this kind of determination, and the X-ray wavelengths which can satisfactorily be used for diffraction purposes are all strongly absorbed by krypton. However, reasonably intense beams of monochromatic neutrons of about 1-Å wavelength are now available, and since they are not absorbed strongly by krypton, they provide a feasible alternative to the use of X rays. In order to investigate the properties of the atomic distributions in liquid krypton more fully, an attempt was made to obtain diffraction patterns of this material at selected temperatures and pressures from low values as close to the triple point as possible up to values as high as those at the critical point.

This program of work required the development of apparatus, with unique characteristics, which would permit containment of the sample at elevated temperatures and pressures. The krypton under study filled a cylindrical volume of 0.660-in. diameter and 1.5-in. height in a cell fabricated from an aluminum single crystal grown especially for this research. This pioneering attempt to meet the difficult problem of sample containment at high pressure proved highly successful, for the cell withstood pressures up to 55 atmos and temperatures as low as 117°K while contributing to cell scattering of neutrons in an amount lower than ever reported by anyone for work of this kind. The cell, housed in an evacuated cryostat, was kept at temperatures ranging from 117°K to 210°K at values constant to within 0.05°K by electronic controlling circuits, and the original charge of krypton was contained without measurable leakage in a closed system for the duration of the experiments.

Using neutrons of 1.05-Å wavelength, diffraction patterns were obtained for liquid krypton under 17 different values of pressure and temperature. The triple point temperature of krypton is 104°K, and its critical point temperature is 210°K. The patterns at 117°K, 133°K, 153°K, 183°K, and 210°K were repeated at least three times to obtain more reliable patterns for use in making further detailed analysis. With an incident beam having a horizontal divergence of 0.5°, the counting rate after correction at the highest

point of the first intensity peak was 5800 cpm at 117°K and 3000 cpm at 210°K. Corrections to these patterns were made for unrelated background, for empty-cell scattering, and for noncoherent background that does not provide information relative to the structure of the liquid. In this way, diffraction patterns were obtained to $(\sin \theta)/\lambda = 0.600 \text{ \AA}^{-1}$ for krypton at the above five temperatures; these patterns showed four well-defined peaks for the lower temperatures and three for the higher ones. Every attempt was made to insure that these corrected patterns represented the neutrons scattered coherently by liquid krypton to as large an angle as was possible under the experimental conditions.

These intensity patterns were then used to compute the corresponding atomic distribution functions for krypton at each of the five temperatures chosen for detailed study. Because it is experimentally impossible to obtain complete patterns with unlimited accuracy, a number of procedures were followed to provide guides toward obtaining the best curves and preparing them for analysis. Both experiment and computation showed there is no appreciable center-of-mass correction necessary in the case of krypton.

Extrapolation of the experimental curve to zero angle and fitting the pattern at large angle to the independent scattering curve introduce uncertainties, and they required special attention. Guides to fitting at large angle were found by applying the sensitive condition that

$$\int_0^{s_m} s^2 i(s) ds = -2\pi^2 \rho_0 \text{ and it was assumed that beyond } (\sin \theta)/\lambda = 0.6 \text{ \AA}^{-1}$$

there were no interference effects in the pattern. Using these guides, the best intensity curves were then used to obtain atomic distributions by Fourier transformation using the computer GEORGE of the Applied Mathematics Division of the Argonne National Laboratory. Since it is possible to find in the distribution functions certain criteria for their probable correctness, several curve fittings and extrapolations were made, and their effects on the distribution curves were observed to see how sensitive the final results were to the arbitrary alterations. Although changes appeared in the distribution curves, none were severe and none indicated through the available criteria any basis for adopting them as superior to the first choices. All distributions gave nondiscrete first peaks characteristic of monatomic liquids. For the five temperatures, the positions of the first peaks and the areas assigned to them (number of nearest neighbors) are as follows: 117°K, 4.02 Å, 8.4 atoms; 133°K, 4.03 Å, 7.9 atoms; 153°K, 4.08 Å, 7.0 atoms; 183°K, 4.10 Å, 6.4 atoms; 210°K, 4.20 Å, 4.0 atoms. The number of nearest neighbors was found to be closely proportional to the density of the liquid.

These distribution curves are useful because (1) they disclose the structure of the liquid, (2) they can be related to the interatomic potentials, and (3) with their help, properties of materials, such as heats of fusion or

of vaporization, can be computed. Before using them in any of these ways, it is essential to assess the reliability of the detailed information they present. This depends upon the fidelity of the experimentally determined intensity curves and upon their subsequent analysis. Since the experimental data were obtained under the best conditions presently available, they are assumed to be correct, although it is recognized that the relative precision of the experimentally determined departures from independent scattering intensity decreases as the scattering angle increases. Nevertheless, reasonably satisfactory duplication of details of intensities in repeated trials gives confidence that these curves are not far from correct over the observable range.

However, there are some questionable procedures in the subsequent analysis and these must be examined. Extrapolation of intensity to zero angle and fitting the intensity curve to the angularly independent free-atom scattering are two possible sources of difficulty, but arbitrarily introduced deviations in these procedures demonstrated the relative insensitivity of the distribution curves to possible errors in these procedures, and it is believed that they can be dismissed as significant sources of unreliability.

If the experimental data were known with unlimited certainty as far as observations had been taken and the zero extrapolation and large-angle fitting made entirely correctly, there still remains a feature of the analysis that can introduce spurious details into the distribution curves. This feature is the finite termination of the diffraction pattern, and its effect has been demonstrated in the analysis of diffraction patterns from crystalline materials as well as from liquids. Recognizing the possibility of spurious effects arising from this cause, extensive tests were made in an attempt to see whether the results presented here suffer appreciably from them. Accordingly, the most intense and best-determined curve was subjected to a series of exploratory procedures intended to provide information in this connection. In one test, the intensity curve was arbitrarily terminated at eight points, giving corresponding distributions that show progressive changes in their details. The slope of the small r side of the peak that represents the nearest-neighbor atoms is one important feature that changes. Plotting the ratio $r(0)/r(\text{max})$ as a function of the termination position shows that reasonable extrapolation to termination beyond presently available experimental limitations leads to a value of this ratio that can be related in an approximate quantitative way to Lennard-Jones potential functions. Furthermore, a similar treatment of results reported elsewhere for argon leads to a value for this ratio very similar to these results. This tends to indicate that, although the present results are probably correct as far as they go, a significant amount of relevant information remains unobserved beyond the point of termination.

Another effect of finite termination is the introduction of ghost peaks adjacent to a prominent real peak, and the separation of the ghost peak from the real peak is related to the point of termination. In the series of distribution curves obtained by arbitrary terminations of the best experimental pattern, ripples do often appear on both sides of the nearest-neighbor peak. These ripples on opposite sides of the main peak are not usually the same shape nor size and their displacements to large r and to small r are not exactly the same, but the trend in their positions follows closely the trend predicted by an approximately appropriate relation. This casts some doubt on the validity of all the small fluctuations on the distribution curves, including the small peak on the longer side of the main peak. The lack of this small peak for the cases of some of the drastic artificial terminations may mean that it is hidden in other features of the curve. It is interesting and undoubtedly significant to note that in the neutron diffraction study of neon at one temperature, no such extra peak appears, but this is shown in the present work to be expected for a radial distribution calculated from an intensity curve terminated as severely as was done in the case of neon. A survey of results with other monatomic liquids is not conclusive, but it tends to indicate that when patterns of grossly inadequate angular extent were used, the extra peak was subdued or absent, whereas when somewhat more diffraction pattern was used the extra peak often appeared in some way.

In further attempts to learn about the extra peak, a modifying factor was applied to the $i(s)$ function to subdue in an artificial way the contribution to the distribution function made by the relatively poorly determined portion of the intensity at large angles, including the point of termination. Though this procedure is not intended to provide a curve in which all its details are to be taken as more correct than those of unmodified curves, nevertheless, this kind of treatment of the severity here used will eliminate features of the distribution curve which originate either from the large-angle part of the intensity curve or from its termination. This strongly subdued all ripple effects over the entire distribution curve. It has not been possible from this to eliminate termination error as a source of these ripples and hence doubt remains of the reality of the extra peak.

It is seen from the distribution curves of Figure 22 that small ripples appear on all of them, being somewhat more prominent in the high-temperature case than in any of the others. If this is assumed to be due solely to a termination effect, it seems at first consideration to be inconsistent with the results of artificial termination tests, for at 210°K the point of termination has in effect been reduced to $(\sin \theta)/\lambda = 0.5 \text{ \AA}^{-1}$ and in the artificial termination tests this did not give rise to a ripple of increased size. However, ripples flanking the main peak are displaced from it by amounts which are in qualitative accord with predictions based on the assumption that they arise from finite termination. Furthermore, if termination is considered to play no part in creating these ripples, then

their reality is based almost wholly on the precise determination of the exact form of the rapidly fading intensity departures at large angles from the free-atom scattering curve, and there is some question whether this part of the curve is known with an accuracy sufficient to establish with certainty the reality of these ripples. Their occurrence in the curves of Figure 30 is not sufficiently in detailed accord with available relations to assign with confidence their origin as wholly due to termination ripples, but, on the other hand, this has not been ruled out as a possible source of at least some of the ripples. It is possible that a more extensive theoretical analysis of details of termination errors will make it possible to assess their contribution to these patterns, or that eventually experimental facilities will be improved so that observations can be carried to large values of $(\sin \theta)/\lambda$.

The distribution curves presented here are the first that have been obtained for liquid krypton, and they are given for five different pressures and temperatures between the triple point and the critical point. The most important information they provide concerns nearest neighbors in this liquid at these different temperatures. They show the trend in nearest-neighbor average distances and average concentrations associated with the first peak, and it is believed that the slopes of the smaller sides of these peaks present a reasonable reliable representation of the trend in these slopes for krypton at different temperatures. Theoretical analysis of these slopes can supply information concerning properties of krypton computed from basic considerations.

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