In addition to the intrinsic levels with spin $\frac{1}{2}+$ and $11/2-$, some rotational levels of the $K=\frac{1}{2}$ and $K=\frac{3}{2}$ bands are shown. The transition from Ir to Au is characterized by a drop in nuclear deformation and by an overcrossing of the $\frac{3}{2}+$ and $\frac{1}{2}+$ intrinsic states. Considering this fact, the generally smooth behavior of the $\frac{1}{2}$, $\frac{3}{2}(K=\frac{1}{2})$, and $5/2(K=\frac{3}{2})$ levels is worth noting. The $11/2-$ level follows this trend not too rigidly and is somewhat low in Ir^{193} and somewhat high in Au^{197}.

ACKNOWLEDGMENTS

We wish to thank Professor J. W. M. DuMond for his interest in this work and Professor S. A. Moszkowski and Dr. E. N. Hatch for helpful discussions.

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Atomic Distribution in Liquid Argon by Neutron Diffraction and the Cross Sections of A^{36} and A^{40}

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The angular distribution of 1.04 A neutrons scattered by liquid argon at 84°K is reported. Small-angle scattering in the pattern is accounted for in terms of isotope incoherence using the same sign for the measured values of the scattering lengths of A^{40} and A^{36}. The transmission cross section of A^{36} was measured for 1.04 A neutrons and found to be 77 ± 9 barns corresponding to a scattering cross section of 73 ± 9 barns. The scattering cross section of A^{40} was measured and found to be 0.36 barn. The scattering curve was transformed to the atomic density distribution $4\pi r^2[\rho(r)-\rho_0]$ for the liquid. The function shows only small oscillations about $-4\pi r^2\rho_0$ for spacings out to 3 A. Beyond this the curve oscillates about zero with an amplitude which decreases with increasing radius. The number of neighbors assigned to the first shell of atoms is $8._2$. From a comparison of the position of the density cutoff and first density maximum with that expected for a Lennard-Jones 12:6 potential, it is concluded that the effective potential in the liquid has a broader bowl than that given by the Lennard-Jones 12:6 potential.

INTRODUCTION

A KNOWLEDGE of the atomic distributions in liquids is of importance for the theory of liquids. It should be possible to calculate all the thermodynamic properties of a liquid from a knowledge of the atomic distribution function and the potential function. The liquid argon atomic distribution function has been previously measured by using x-rays,[1–4] and these results have been summarized in a review article by Gingrich.[5] The atomic distributions in the liquid and the vapor have been studied extensively by x-rays over a wide range of pressure and temperature by Eisenstein and Gingrich.[4] They reported radial distribution functions for spacings out to 8 A.

More recently the structure of liquid argon at 86.3°K has been measured by means of neutrons.[6] The atomic distribution was reported for radial separations out to 20 A. The neutron scattering pattern contained considerable small-angle scattering which could not be attributed to incoherence on the basis of known nuclear data. In transforming the measurements, it was assumed that all the scattering was coherent and that the formula of Debye[7] and of Zernicke and Prins[8] could be applied to the scattering pattern.

We have measured the scattering from liquid argon with higher statistical accuracy at 84°K, using 1.04 A neutrons, and have shown that the small-angle scattering is real and can be attributed to isotope incoherence arising from a large scattering cross section for A^{36}. The measured scattering pattern has been transformed by using the formula of Debye and of Zernicke and Prins, modified to allow for the incoherence. The radial distribution function which was calculated out to 20.0 A is an oscillating function whose amplitude decreases monotomically with increasing r. The positions of the first density maximum and the point where the atomic density rises from zero are discussed in relation to some two-particle potentials for argon.

APPARATUS

The measurements of the angular distribution of scattered neutrons were made by using one of the Chalk River neutron spectrometers with the arm recording in the antiparallel rocking position and with the NaCl monochromating crystal set to diffract neutrons of wavelength 1.04 A. The liquid argon was held in the 5 in. diameter cassette previously described.[6] The scattered intensities were measured at 84°K over the

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[1] W. H. Keesom and J. de Smedt, Proc. Acad. Sci. Amsterdam **25**, 118 (1922); **26**, 112 (1923).

[2] K. Lark-Horovitz and E. P. Miller, Nature **146**, 459 (1940).

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

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[6] Henshaw, Hurst, and Pope, Phys. Rev. **92**, 1229 (1953).

[7] P. Debye, Ann. Physik **46**, 809 (1915).

[8] F. Zernicke and J. Prins, Z. Physik **41**, 184 (1927).

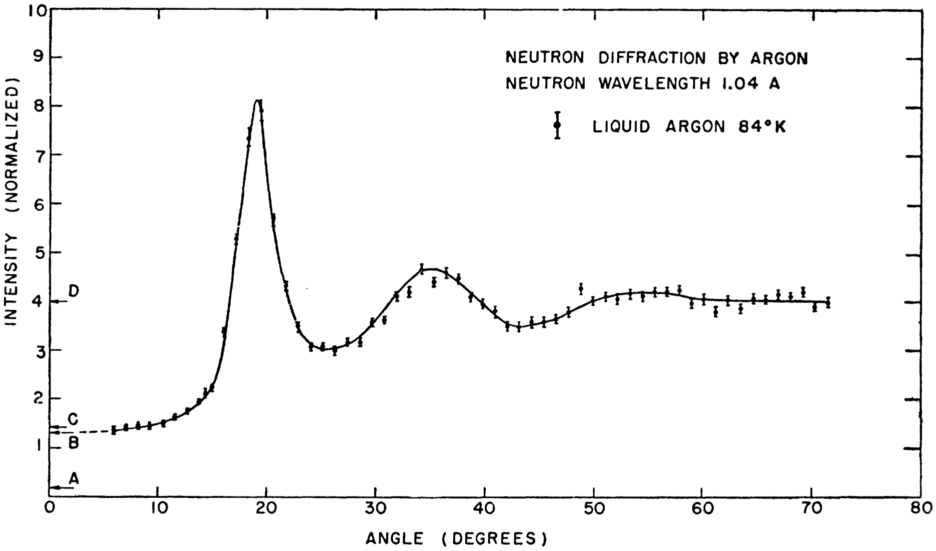

FIG. 1. The angular distribution of 1.04 A neutrons scattered by liquid argon at at 84°K. The vertical bars at each point represent the statistics based solely on the total number of counts. Arrows A, B, C, and D show, respectively, the calculated zero-angle scattering for complete coherence, the zero-angle scattering extrapolated from the measurements at small angles, the extrapolated zero-angle scattering measured for the solid, and the level of the large-angle scattering.

angular range 5° to 70°. The total number of counts for a fixed number of monitor counts was recorded at about 60 equally spaced points in the above angular range.

EXPERIMENTAL RESULTS

The angular distribution of 1.04 A neutrons scattered by liquid argon at 84°K is shown in Fig. 1. The scattered intensities are corrected for background, resolution, double scattering and for change in the effective scattering volume with angle. The vertical bars shown on each point represent the statistical error based solely on the total number of counts.

Because argon is a classical liquid, the small-angle coherent scattering should be accurately represented by the formula:

$$L_0 = NkTX_T, \tag{1}$$

where L_0 = zero angle structure factor, X_T = isothermal compressibility, and N = particle number density in atoms/cc. The arrow designated by A on the ordinate scale of Fig. 1 represents the zero-angle scattering calculated from Eq. (1) if one assumes that all the scattering at large angles is coherent. The arrow B represents the extrapolation of the curve to zero angle while the arrow D represents the level of the large angle scattering. The arrow C represents an extrapolation to zero angle, of the measured small-angle scattering from the solid. These measurements confirm the existence of the small-angle scattering reported for liquid argon in our earlier publications.[6]

It is seen from Fig. 1 that the measured small-angle scattering B is in excess of A, that predicted by Eq. (1). The zero-angle scattering for the solid is again much larger than the zero-angle scattering predicted from the above formula. It is to be noted that the observed zero-angle scattering for the solid is higher than that in the liquid even though the calculated zero-angle scattering from Eq. (1) is smaller in the solid than in the liquid. This difference is probably due to the difference in bulk density between the solid crystals and the liquid which is of the order of 15%.

Because the isothermal compressibility cannot account for the observed zero-angle scattering from the liquid and solid, it was concluded that this excess small-angle scattering is incoherent in origin. The height of B is a measure of the incoherent scattering cross section, while the height of D represents the total scattering cross section. The difference $D-B$ is a measure of the free-atom coherent scattering cross section.

The incoherent scattering may arise from three sources (a) impurity, (b) spin, or (c) isotope incoherence. Measurements were made to check that the incoherence was not caused by impurity. The argon supplied by the Matheson Company Limited[9] was purified by passing it over uranium chips heated to 950°C, over uranium chips heated to 250°C, and then through a trap immersed in liquid nitrogen before the gas was liquified in the cassette. The angular distribution of neutrons scattered by this purified argon was measured and it was found that within experimental error the scattering pattern was the same as for the unpurified argon. Spin incoherence was considered improbable because A^{40} is an even-even nucleus. Accordingly, to determine whether the small-angle scattering could be attributed to isotope incoherence, the transmission cross section of argon gas enriched in A^{36} was measured. The analysis of the gas is given in Table I.

The transmission of the gas was measured in a 32.5 in. long cassette having a $\frac{3}{16}$ in. internal diameter. A

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[9] This argon was stated to have a purity of 99.9%, the main impurity being nitrogen with the hydrogen and oxygen content each being less than 0.002%.

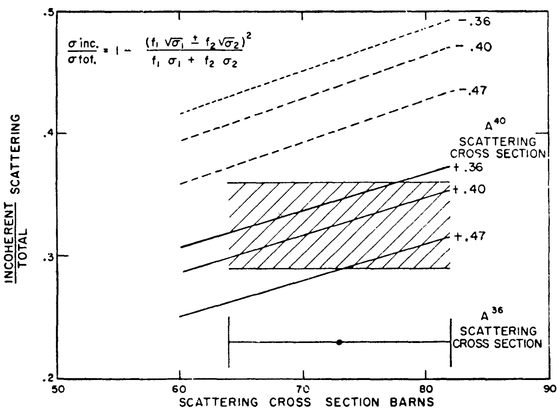

FIG. 2. The ratio of the incoherent to total scattering cross section for liquid argon calculated for three values of the A^{40} scattering cross section is shown plotted against the scattering cross section of A^{36}. The solid sloping lines represent the calculated ratios of incoherent to total scattering when one assumes that the signs of the scattering length of A^{36} and A^{40} are the same, while the dotted lines represent the ratios when one assumes that the signs are opposite. The shaded area represents the limits for the ratio of incoherent to total scattering given by the ratio of small-angle to large-angle scattering of the liquid.

side tube, which had a bulb of volume 0.26 cc attached to one end, was attached to the cassette. Two sheets of cadmium, 0.030 in. thick, each having a central hole $\frac{1}{8}$ in. in diameter were attached one to each end of the cassette and defined the neutron beam.

The break seal flask containing the argon, and the cassette, were attached to a vacuum system and the cassette was thoroughly evacuated. One end of the cassette was cooled to liquid helium temperature, and the argon allowed to solidify in the cassette. The volume of gas transferred, measured[10] at the completion of the transmission measurements, was 77.8±1 cm^3 at NTP.

The transmission of the gas sample was measured by using 1.04 A neutrons on one of the Chalk River neutron spectrometers set in the zero-angle position. The numbers of neutrons transmitted in one-minute intervals were recorded. A series of measurements were made with the side bulb at room temperature and then with the side bulb at liquid nitrogen temperature. The measurements were continued until about 10^6 counts had been accumulated for each condition. The measurements were repeated with 0.030 in. cadmium in the beam in order to correct for the epicadmium neutrons. The number transmitted through the cadmium was small amounting to less than 1% of those transmitted without the cadmium in the beam. The ratio of the transmission of the 1.04 A neutrons for the bulb at 77.5°K and 293°K was 0.850.

The transmission cross section for the argon was deduced from the measured value of the change in transmission of the sample with and without liquid nitrogen on the side bulb, and the change in concentration of argon in the tube for these conditions. At 293°K the pressure of argon in the cassette was calculated from the volume of the cassette and the volume and analysis of the gas. The pressure of argon with the bulb at 77.5°K was taken as the vapor pressure of solid argon at that temperature. It was assumed that the amounts of oxygen and nitrogen in the cassette remained unchanged with change in temperature of the bulb because of their low partial pressures. The cross section deduced for the argon was 19.6 barns.

TABLE I. Analysis of argon gas enriched in A^{36}.

Isotope	Molecular percent
A^{40}	82.46
A^{38}	0.33
A^{36}	16.63
$N^{14}N^{14}$	0.49
$N^{14}N^{15}$	0.06
$O^{16}O^{16}$	0.03

The transmission cross section for a specimen of liquid argon at 86°K having normal isotopic concentration, was then measured for 1.08 A neutrons using a 5 in. thick liquid sample. The ratio of the transmission with the cassette full of liquid and evacuated was 0.77 corresponding to a transmission cross section of 0.96 barn. Subtracting 0.35 barn[11] for the absorption cross section of A^{40} for 1.08 A neutrons, a value of 0.61 barn was assigned to the combined effect of the scattering cross section of A^{40} and the total cross section of A^{36}. By a method of successive approximations, the total cross section of A^{36} and the scattering cross section of A^{40} was calculated. A value of 0.36 barn was deduced for the A^{40} scattering cross section while 77±9 barns was found for the A^{36} transmission cross section, which yields 73±9 barns for the scattering cross section when corrected for the absorption cross section.[12] The various measured values of the cross sections of argon are listed in Table II. The scattering cross sections of A^{40} were deduced from the measurements on normal argon by correcting the measurements for the cross section of A^{36}. The average of the scattering cross sections for A^{40} is 0.45 barn.

ANALYSIS OF THE MEASUREMENTS

The relative signs of the scattering lengths of A^{40} and A^{36} together with their respective cross sections determine the ratio of the incoherent to total scattering. This ratio is closely approximated by the ratio of zero-angle to large-angle scattering for a solid and, under certain conditions, for a liquid.

The ratio of incoherent to total cross section is given

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[10] I should like to thank Mr. M. Tomlinson of the Radiation Chemistry Section at Chalk River for these measurements.

[11] F. C. W. Colmer and D. J. Littler, Proc. Phys. Soc. (London) **A63**, 1175 (1950).

[12] G. E. McMurtrie and D. P. Crawford, Phys. Rev. **77**, 840 (1950).

TABLE II. Neutron cross section for argon (barns).

Reference	Normal argon σ_T	σ_a	σ_s	σ_{coh}	A^{40} [i] σ_s	A^{36} σ_T	σ_a	σ_s
Colmer and Littler[a]		0.62[g]						
Melkonian[b]			0.68		0.43			
Harris[c]			0.8		0.55			
McReynolds[d]				0.5 ± 0.1	0.45 ± 0.1			
McMurtrie and Crawford[e]							6.5 ± 1[g]	
Present paper	0.96[f]		0.61		0.36			
Present paper						77 ± 9[h]		73 ± 9
Average					0.45			

[a] See reference 11.
[b] E. Melkonian, Phys. Rev. **76**, 1750 (1949).
[c] See reference 13.
[d] A. W. McReynolds, Phys. Rev. **84**, 969 (1951).
[e] See reference 12.
[f] 1.08 A neutrons.
[g] Average cross section from pile spectrum neutrons.
[h] 1.04 A neutrons.
[i] σ_s deduced for A^{40} from the cross sections of normal argon and A^{36}.

by:

$$\Delta=\frac{\sigma_{\text{incoh}}}{\sigma_{\text{total}}}=1-\frac{(f_1\sigma_1^{\frac{1}{2}}\pm f_2\sigma_2^{\frac{1}{2}})^2}{f_1\sigma_1+f_2\sigma_2}, \tag{2}$$

where f_1 = isotopic concentration of A^{40}, f_2 = isotopic concentration of A^{36}, σ_1 = scattering cross section of A^{40}, and σ_2 = scattering cross section of A^{36}. Using 0.36, 0.40, and 0.47 barn for the scattering cross section of A^{40}, the ratio of the incoherent to total scattering in natural argon was calculated for various values of the A^{36} scattering cross section in the range 63 to 80 barns. The ratios were calculated for the signs of the scattering lengths (a) the same and (b) opposite. The results are plotted against the A^{36} scattering cross section in Fig. 2. The dotted lines represent lines of constant A^{40} cross section in which the sign of the scattering lengths of A^{40} and A^{36} are opposite while the solid lines represent the results of the calculations assuming the same signs. The shaded band represents the limits of the measured ratio of incoherent to total scattering obtained from the ratio of the small-angle to large-angle scattering in the liquid. The horizontal limits of this shaded area represent the uncertainty in the A^{36} scattering cross section.

From the figure, it may be seen that if the scattering cross section of A^{40} is taken as the average value (i.e., 0.45 barn) given in Table II, then the measurements can only be fitted by assuming that the sign of the scattering lengths of A^{36} and A^{40} are the same. It would be just possible to fit the results by using a value of 0.55 barn,[13] assuming opposite signs for the scattering lengths. This measurement appears to be high, however, and our conclusion is that the signs of the scattering lengths are similar.

The conditions under which the measured angular distributions of the neutrons scattered from the liquid may be transformed to the atomic distribution have been discussed previously.[6,14] For an angular distribution consisting of a coherent and incoherent portion, the formula of Debye and of Zernicke and Prins applies only to the coherent portion. If it is assumed that the incoherent scattering is isotropic, the formula connecting the atomic distribution with the scattered intensities may be written as:

$$4\pi r^2[\rho(r)-\rho_0]=\frac{2r}{\pi}\int_0^\infty si(s)\sin(rs)ds, \tag{3}$$

where r = distance from an atom chosen as center, $\rho(r)$ = atomic density at a distance r, ρ_0 = mean atomic density of the liquid, $s=(4\pi/\lambda)\sin(\varphi/2)$, λ = neutron wavelength, φ = angle of scattering, $i(s)=(I_s-I_\infty)/I_\infty(1-\Delta)$, I_s = intensity of coherent scattering for the value s of the variable, I = value of I_s for $s=\infty$, and Δ = value of the incoherent scattering which is assumed to be isotropic.

A first method for calculating Δ is from Eq. (2) using measured values of the isotopic concentrations and cross sections.

A second method is to extrapolate the scattering curve to zero angle. This zero-angle scattering, when corrected for the coherent small-angle scattering given by Eq. (1) and divided by the scattering at large angles, gives Δ, the ratio of the incoherent scattering to total scattering.

A third method is based on the fact that for monotomic liquids the atomic density is zero out to the nearest distance of approach of two atoms. The scattering curve of Fig. 1 was transformed to the atomic density distribution $4\pi r^2\rho(r)$ for r in the range 0 to 3.4 A using Eq. (3). Three transforms were calculated, the first for a value of $\Delta=0.300$, the second for $\Delta=0.325$, and the third for $\Delta=0.350$. Each transform was normalized so that $\rho(r)\rightarrow0$ as $r\rightarrow0$ by choosing I_∞ such that $-2\pi^2\rho_0=\int_0^{S_{\max}}s^2i(s)ds$, where $S_{\max}$ is the last measured[6] value of s. In the first transform, the mean value of the atomic density was less than zero while that for the third was greater than zero. The second

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[13] S. P. Harris, Phys. Rev. **80**, 20 (1950).
[14] D. G. Hurst and D. G. Henshaw, Phys. Rev. **100**, 994 (1955).

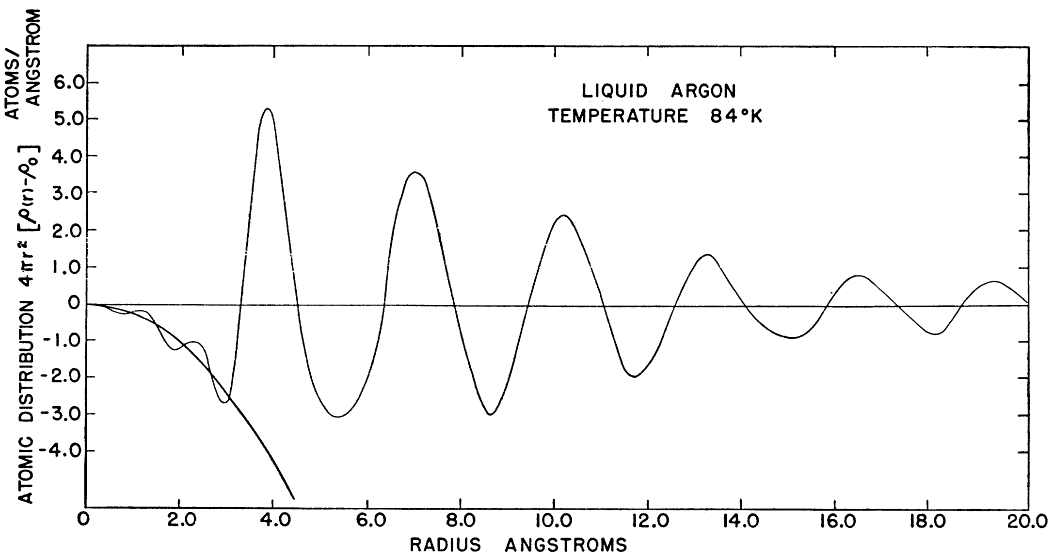

FIG. 3. The transform $4\pi r^2[\rho(r)-\rho_0]$ for liquid argon. The smooth curve is $-4\pi r^2\rho_0$, where ρ_0 is the average density equal to 2.13×10^{-2} atom per cubic angstrom. The main pattern is a series of smooth oscillations which decrease with increasing radius. Only small oscillations occur for $r<3.0$ A. These are certainly spurious.

closely approximated to the zero of density which showed that the value of $\Delta=0.325$ was the best fit to the results. This value of Δ agreed within experimental error with that calculated by Eq. (2) and with that obtained from an extrapolation of the small-angle scattering to zero angle. This was taken as evidence to show that the three methods are consistent.

DISCUSSION OF RESULTS

The radial distribution function $4\pi r^2[\rho(r)-\rho_0]$ was calculated[15] by using $\Delta=0.325$ for $0\leq r\leq 20.0$ A in steps of 0.2 A. The result is shown in Fig. 3. For small r the function $4\pi r^2[\rho(r)-\rho_0]$ oscillates about $-4\pi r^2\rho_0$, rising rapidly at 3.05 A to a maximum at 3.81 A. The small oscillations for $r<3.0$ A are certainly spurious and arise from experimental error and the relatively small range of s over which the measurements could be made. These oscillations presumably extend to larger r but their effect is small compared to the main density fluctuations. Beyond 3.0 A the curve oscillates about zero with an amplitude which decreases with increasing r. The amplitude falls from a value of 5.35 atoms/A at 3.8 A to 0.65 atom/A at 19.3 A, thus showing that the degree of order in the liquid rapidly decreases with increasing radius. The spacing between peaks is nearly constant, changing from 3.2 A in the region of 5 A to 3.0 A in the region of 18 A.

The atomic density distribution is shown in Fig. 4 together with the average atomic density $4\pi r^2\rho_0$. The first maximum occurs at 3.86 A. The number of neighbors in the first shell of atoms may be calculated from an integration of this curve but there is some latitude in the choice of a criterion for the division of atoms into shells. If a symmetrical peak about the maximum in $4\pi r^2\rho(r)$ is assumed, the number of neighbors is calculated to be 8.5 while if a symmetrical peak is taken in the $4\pi r\rho(r)$ curve, the number of neighbors is calculated to be 8.0 atoms. This number is somewhat lower than the 10.2 to 10.9 atoms found by x-rays[4] for liquid argon at 84.4°K but in agreement with the value found by neutrons[6] at 86.3°K. In solid argon, which is a face-centered cubic structure, there are 12 nearest neighbors while our measurements indicate that the liquid has about $8._2$ atoms in the first shell for temperature very near the freezing point. On melting, there is a 14% change in density while the number of neighbors changes by ~32%, which indicates that the arrangement of atoms in argon changes during the solid to liquid transition.

Because the potential energy per atom in the liquid may be calculated from a knowledge of the radial distribution function and the effective two-particle potential function of the liquid, it is of interest to determine whether two-particle potentials generally assumed applicable to argon gas may be applied to the atoms in a liquid. The first maximum and the point where the density distribution rises from zero (density cutoff) are related to the minimum and the zero of the effective two-particle potential in the liquid. In a classical solid or solid having small zero-point motion, the spacing between nearest neighbors at absolute zero should approximately correspond to the minimum of the effective potential. For a liquid the first density maximum would be expected to be just outside the minimum of the potential. The density cutoff should lie in the region of the zero of the effective two-particle potential in the liquid.

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[15] The Fourier transforms were calculated on Ferut by the Computation Center, University of Toronto.

An estimate of the position of this density cutoff relative to the zero of a two-particle potential function has been made by Lee-Whiting.[16] He fitted a Morse potential to the Lennard-Jones 12:6 potential[17] and calculated the wave-mechanical density for two argon atoms in the ground state, and in the fifth excited state which is just bound. The radius of the effective density zero for the ground state was 0.1 A greater than the zero of the potential while that for the fifth excited state was 0.05 A less than the potential zero. From these calculations it is possible to say that the density cutoff should lie within ±0.1 A of the zero of the potential function. Thus by comparing the position of the first maximum and the position of the density cutoff with the spacing of the minimum and zero of two-particle potentials, it should be possible to determine how well these potentials represent the effective two-particle potential in a liquid.

The nearest distance of approach for 2 atoms in the liquid is the point at which the radial distribution function is zero. In Fig. 4 the zero of density is found at 3.05 A. The position of this zero is somewhat dependent upon the treatment of the diffraction curve before its transformation. In particular, it depends upon the value of Δ of Eq. (2) which gives the amount of scattering which is taken to be incoherent in origin. As was discussed earlier, the transform $4\pi r^2\rho(r)$ was calculated for 3 values of Δ equal to 0.300, 0.325, and 0.350. The nearest distance of approach for two atoms was found at 3.02_5 A, 3.05_0 A, and 3.07_5 A, respectively, showing that this spacing is insensitive to the amount of incoherence assumed. The expected error from this would be ~1%. The estimated total error is then given as ±2% by adding another ±1% for uncertainty in the determination of the neutron wavelength. Using the limits given by these errors, the density zero is given as 3.05±0.06 A.[18] The ratio of the spacing at the density zero to that at the density maximum is 0.79. Thus the bowl of the effective potential in the liquid is wider than that of the Lennard-Jones 12:6 potential where the ratio is 0.894. The width of the bowls of the other potential functions used to represent the two-particle potential of gaseous argon are also too narrow.

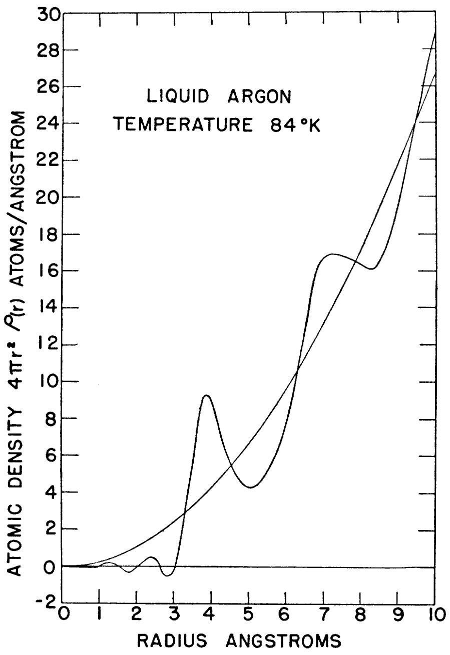

FIG. 4. The radial distribution function $4\pi r^2\rho(r)$ deduced from the curve of Fig. 3. The parabolic curve is the average atomic density $4\pi r^2\rho(0)$.

This conclusion is in agreement with that of Kihara[19] who discussed the stability of a system of symmetrical particles in which the zero-point motion does not play an essential role. He concluded that in order that solid argon might be face-centered cubic, the real intermolecular potential for a rare gas must have a wider bowl and a harder repulsive wall than the Lennard-Jones 12:6 potential.

ACKNOWLEDGMENTS

The author would like to thank Professor W. W. Watson and Dr. J. M. Corbett of Yale University for supplying the sample of A^{36} gas with which the cross section of A^{36} was determined. Thanks are due to Dr. D. G. Hurst, Dr. N. K. Pope, and Dr. B. N. Brockhouse for helpful discussions.

Note added in proof.—It should also be pointed out that the position of the density cutoff lies well inside the zero of the two particle potentials given by Whalley and Schneider[17] while the first density maximum tends to lie at a spacing which is less than the position of the minimum of these potentials.

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[16] G. E. Lee-Whiting (private communication).

[17] E. Whalley and W. G. Schneider, J. Chem. Phys. **23**, 1644 (1955).

[18] This value is somewhat smaller than the value of 3.24 A reported by Eisenstein and Gingrich[4] for liquid argon at 84.4°K. It is interesting to note that whereas they reported the first maximum in $4\pi r^2\rho(r)$ at 3.79 A, the analysis of Fig. 2 shows a peak at 3.86 A. Thus the peak reported here is slightly broader and the position of its maximum is more in accord with the measurements in the solid where the first density maximum is at 3.82 A.

[19] T. Kihara, Revs. Modern Phys. **25**, 831 (1953).