Radial Density Functions for Liquid Mercury and Lead

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The effects of data termination and systematic errors on the radial distribution functions of liquids obtained from x-ray diffraction data are investigated with the aid of a computer. A general procedure for the elimination of spurious detail is presented, and new data for liquid mercury and lead are analyzed. Comparisons of radial distributions for the solid and the corresponding liquid near the melting temperature show that the radial density functions for the liquid and the corresponding crystalline solid are strikingly similar, whereas liquid lead is different from liquid mercury. The liquid structure may be described by starting with the structure of the polycrystalline solid and specifying the following parameters: The mean nearest-neighbor distance r_1 ; the average density of the liquid ρ_0 ; the critical correlation distance d; and the mean-square relative displacements between atom pairs, σ^2 . The σ^2 vary with pair separation and include both thermal vibrations and diffusive motions. The mean nearest-neighbor distance in the liquid is shown to be smaller than in the solid.

I. INTRODUCTION

THE radial distribution function may be derived from a transform of the diffracted x-ray intensity. Although the procedure is straightforward, the final result is subject to a number of errors arising from such factors as misalignment, uncertainty in the shape of the form factor, beam divergence, absorption effects and from the termination of the experimental data at finite scattering vectors. The presence of such errors probably accounts for the differences between various sets of published data. The variations in the available results and the lack of error analyses make detailed interpretations of the existing radial density functions questionable.

It is difficult to obtain raw distribution functions free from error, and it is thus necessary to develop datareduction techniques which include methods of error analysis. We have devised a method for treating errors in the experiment by means of a digital computer, and the procedure is applied to new measurements on liquid mercury and liquid lead. We show that the liquid structures are related in a systematic way to the structures of the corresponding solids. Furthermore, liquid lead is definitely different from liquid mercury. We finally attempt to relate the liquid quantitatively to the corresponding solid structures by specifying the atomic displacements, a characteristic correlation distance, a lattice parameter, and the density of the liquid.

II. EXPERIMENTAL PROCEDURE

Diffraction data were obtained with a spectrometer in which the specimen is horizontal and the source and detector move in such a way as to maintain focusing conditions.¹ The mercury was contained in a $2\frac{1}{2}$ in. diam boat inside a chamber filled with helium. The large specimen diameter minimized the curvature at the central portion of the pool. The crucible used for the lead provided a surface $2 \times 1\frac{1}{2}$ in. Specimen heights were checked by means of particles of MgO floating on the surface, and other features of the alignment were verified by using polycrystalline and single-crystal samples. Most of the data were obtained with $MoK\alpha$ radiation, using a silicon crystal monochromator in the diffracted beam. $CoK\alpha$ and $CrK\alpha$ were also used to check the low-angle region for mercury. Adjustable slits and 3° lateral Soller slits were used to limit the divergence and to remove extraneous scattering from the windows; the resultant width at half maximum for a powder peak at $\sin\theta=0.3$ was 0.001. A scintillation-counter and pulse-height-analyzer combination was used as the detector.

The post-specimen monochromator removes the fluorescent radiation and the Compton modified scattering at high scattering angles. The wavelength acceptance of the monochromator was measured by observing the (111) reflection from a silicon single crystal irradiated with white radiation, and also by measuring the Compton scattering in silicon. Both methods yielded the same cut-off angle for Compton radiation, which occurred at $\theta=21^\circ$. At lower angles the Compton scattering is less than 1% of $|f|^2$ for both lead and mercury, and can be neglected entirely.

Data were obtained a number of times for each liquid with the diffractometer running first in one direction and then in the other to compensate for slow variations in the x-ray intensity and in the detector system.

III. ANALYSIS OF THE DATA

The intensity of x rays scattered by a monatomic liquid at angles not very close to the origin is related to the radial distribution function as follows:

$$F(k) = k \left\{ \frac{I}{f^2} - 1 \right\} = \int_0^\infty G(r) \mathrm{sin} k r dr , \qquad (1)$$

where I is the x-ray intensity, electron units per atom, f the atomic scattering factor, r the radial distance from an atom at an arbitrary origin; G(r) equals $4\pi r(\rho - \rho_0)$

^{*} Supported by the U. S. Office of Naval Research.

¹ R. Kaplow and B. L. Averbach, Rev. Sci. Instr. 34, 579 (1963).



FIG. 1. Distribution function and resultant intensity function used in the error analysis.

and is the radial distribution function; k equals 4π $\sin\theta/\lambda$; ρ is the atomic density, atoms per unit volume, at a radial distance r, and ρ_0 is the average atomic density. The radial density, $J(r) = 4\pi r^2 \rho dr$, describes the number of atoms in a spherical shell between r and r+dr. A Fourier inversion of Eq. (1) yields,

$$G(r) = -\frac{2}{\pi} \int_0^\infty F(k) \sin kr dk \,. \tag{2}$$

In practice, we observe the scattered intensity I_m in arbitrary units

$$I_m = IP(\theta)/A , \qquad (3)$$

where $P(\theta)$ is the polarization factor, and A is a normalization constant. The value of I approaches f^2 at large values of k, and a plot of $I_m/P(\theta)f^2$ should thus approach a limiting value 1/A. This is a convenient method of obtaining the normalization constant when only coherent radiation is significant. However, the normalization is subject to systematic errors, and the values of f are sometimes uncertain at large angles. In addition, we do not have experimental data for F(k)from zero to infinity, and the effects of the termination on the transform must also be considered.

We illustrate the effects of errors by starting with a known function G(r) shown in Fig. 1. This is actually the final result obtained for liquid mercury at 25°C, but we consider it as the starting point of the error analysis. The corresponding function F(k) was obtained by carrying out the integration of Eq. (1) by means of a computer, and this is also shown in Fig. 1. This is the true intensity function. Errors in the intensity function are now introduced and the resultant effects on the function G(r) are investigated.

A. Normalization Error

Many authors have discussed normalization procedures and the errors introduced by improper normalization.^{2,3} If the Compton modified contribution is negligible, the effect of choosing the wrong normalization constant for the experimental intensity is easily seen.

Let us assume that the normalization constant is one percent greater than the correct value. The corresponding error in F(k) becomes

$$\Delta F = (\Delta A/A)k(I/f^2 - 1) + (\Delta A/A)k, \qquad (4)$$

where $(\Delta A/A)$ is the fractional error in A. This error function is shown in Fig. 2(a). The resultant G(r) is then the true function modified by a change in scale plus the transform of a ramp of slope $\Delta A/A$; the error in G(r) is shown in Fig. 3(a). The transform of the ramp has the form.

$$\Delta G = \frac{\Delta A}{A} \left[\frac{\sin k_m r}{r^2} - \frac{k_m \cos k_m r}{r} \right], \qquad (5)$$

where k_m is the maximum value of k. The error function ΔG exhibits sharp oscillations at values of r close to zero, and the absence of these sharp oscillations is thus a useful criterion for determining the correct value of A.

B. Errors in Scattering Factors

There is no certainty as to the form of the error caused by errors in the scattering factors, but it is



FIG. 2. Variation in F(k) arising from errors in normalization and scattering factors.

² J. Krogh-Moe, Acta Cryst. 9, 951 (1956).
 ³ J. Bienenstock, J. Chem. Phys. 31, 570 (1959).



FIG. 3. Variation in G(r) arising from normalization, scattering factor and termination errors.

probable that it has the form, $\Delta(I/f^2) = (I/f^2)\epsilon$, where ϵ is a slowly varying function of k. Alignment and absorption errors would probably have a similar form. The resultant error in F may be written as

$$\Delta F = \epsilon k (I/f^2 - 1) + \epsilon k. \tag{6}$$

If the normalization criterion, which is described above, is used when a slowly varying error is present, a partially compensating normalizing constant will be chosen. The net effect on F is then

$$\Delta F = (\epsilon + \Delta A/A)k(I/f^2 - 1) + (\epsilon + \Delta A/A)k.$$
(7)

The error in G(r) due to the first term in Eq. (7) will consist of a convolution of the cosine transform of $(\epsilon + \Delta A/A)$ with the true G(r). Since $(\epsilon + \Delta A/A)$ is slowly varying, the effect of the convolution will again be primarily a scale change. The second term $(\epsilon + \Delta A/A)k$, will cause a more obvious error, since its transform will be most significant below the first peak in G(r). For purposes of illustration we assume an error, $\epsilon = 0.15 \exp(-0.005k^2)$. The error in F(k), after renormalization, is shown in Fig. 2(b) and the corresponding error in G(r) is shown in Fig. 3(b). It may be noted that the principle error in G(r) occurs at small values of r.

In a real distribution function we expect the first peak in G(r) to occur at a well-defined distance, as shown in Fig. 1. In the region before the first peak, $G(r) = -4\pi r\rho_0$, and the errors will appear as modulations of a straight line. If we consider only the small r region of G(r), we may define a function ΔG which is the difference between the experimental value and a straight line, G(r) = -Dr. If we choose the proper value of the slope D the transform of ΔG will approximately equal $k(\epsilon + \Delta A/A)$ and ΔF can be obtained by multiplying by I/f^2 . The criterion for choosing D is that the resultant error transform should not contain rapid oscillations near k=0. It will be noted that ρ_0 is not a required parameter of the error analysis; thus, the final value of the initial slope, which should be $4\pi\rho_0$, is an experimental measure of the average density.

C. Termination Error

The transform in Eq. (2) requires data from k=0 to $k=\infty$. A lack of exact data at small values of k is not too serious, however, since F(k) is very small in this region. The termination of data at $k_{\max} < \infty$ introduces spurious detail in the resultant G(r).

Although the effects of data termination in transform analyses have been discussed by many authors,⁴ no feasible procedure has been proposed previously to correct for those errors. In arriving at a true function G(r)from experimental data, we make use of two criteria: (1) a transform of G(r) must reproduce the measured intensity function; (2) in the absence of other errors, the function G(r) in the region below the first peak must be linear.

We illustrate the termination error by limiting the function F(k) in Fig. 1 to k < 10 Å⁻¹. The resultant error in G(r) is shown in Fig. 3(c), and it is interesting to note that the greatest error occurs in the vicinity of the first peak, where it can cause considerable confusion. The effects of terminating F(k) at 6, 10 and 14 Å⁻¹ are shown in Fig. 4. From the trend indicated by the three terminations, it is possible to see the direction of the necessary corrections.

We make the termination correction as follows. A first approximation $G^{(E)}$ is obtained by transforming the normalized data $F^{(E)}$ for three or more termination points. The function $G^{(E)}$ is corrected by following the trend of the successive termination effects and removing the obvious irregularities and the oscillations below the first peak. The corrected function $G^{(C)}$ is then transformed to produce the function $F^{(C)}$, which may be compared with the experimental function $F^{(E)}$. $F^{(C)}$ and $F^{(E)}$ will differ in two ways: (1) they may be different in

⁴ For a partial review, see K. Furukawa, Rept. Progr. Phys. 25, 395 (1962).



FIG. 4. Effect of data termination on distribution function.

the region $0 < k < k_m$, indicating that the function $G^{(C)}$ is not consistent with the experimental data, and (2) the function $F^{(C)}$ will extend beyond k_m , since it is computed from $G^{(C)}$ rather than measured experimentally. In general, $F^{(C)}$ will not coincide with $F^{(E)}$ on transforming the first trial value of $G^{(C)}$, but it is usually not obvious how $G^{(C)}$ should be changed from an observation of $\lceil F^{(E)} - F^{(C)} \rceil$.

The new value $F^{(C)}$ is then terminated at k_m and transformed to give a new distribution function. This distribution function contains a termination error, which is obtained by subtraction and used to correct the experimental function, $G^{(E)}$. The corrected $G^{(E)}$ may be compared with $G^{(C)}$ and the comparison will indicate the alteration required in $G^{(C)}$. The procedure is repeated until the match is arbitrarily good. The transform of the final $G^{(C)}$ is used to extend $F^{(E)}$. At this point we have a function F(k), which matches the experimental values up to k_m , and extends beyond k_m to large values of k. This extended function may then be transformed to give a final value of G(r) which is free from spurious detail, and consistent with the experimental data.

Figure 4 illustrates the feasibility of this procedure. In 4(a) we show G(r) obtained by termination of the F(k) in Fig. 2 at values of 6, 10, and 14 Å⁻¹. Each of the curves in Fig. 4(a) was analyzed by the procedure described above, and the results for these analyses are shown in 4(b); the final curves coincide exactly and reproduce the original value of G(r) shown in 1(a).

We have further tested the sensitivity of the procedure by changing the shape of the leading side of the first correlation peak in the assumed $G^{(C)}$ to a Gaussian with the same half-width at half-maximum as the true function. Even this small change in peak shape resulted in an obvious lack of fit, since the termination error with a Gaussian leading edge is very different than the experimental one. It is, in fact, the extreme sensitivity of the termination error to the shape of the first peak that makes the method useful.

Other attempts to deal with the termination error have depended on the use of exponential damping factors to mask the spurious oscillations. Damping factors, however, severely change the shape of the resulting correlation function and thus make subsequent interpretation uncertain.

The method outlined above yields a G(r) function which is consistent with the experimental data. Unlike the initial result, however, it is a physically plausible solution. The shape is correct below the first peak, and the corresponding intensity function extends smoothly beyond k_m , rather than dropping abruptly to zero. The key feature of the method is the extension of F(k)beyond k_m in such a way that both the extension and the resultant G(r) are physically reasonable. G(r) is not unique in a mathematical sense, but we do not believe it possible to obtain another function, which is significantly different and yet satisfies the necessary criteria.

D. Combined Errors

We have considered the errors separately for clarity. In practice these errors are combined, but their different forms allow them to be separated. A normalization error causes a very large peak close to r=0. An $(I/f^2)\epsilon$ error is also apparent in the region below the first peak and generally decreases with increasing r in that range. The termination error results in oscillations with an approximate period given by $2\pi/k_m$ contained within a smooth envelope which has a maximum amplitude in the vicinity of the first peak. After obtaining the best normalization constant, it is helpful to terminate F(k)at several values of k less than k_m and to observe the resultant effects on G. This makes it easier to correct for the termination error first and to then analyze the remaining oscillations at small r in terms of other errors. Several iterations may be necessary before a final value of G(r) is obtained. Though many transforms are required, the availability of electronic computers and suitable programs⁵ makes the procedure entirely feasible.

The efficacy of the correction procedure was tested by introducing simultaneously normalization, $(I/f^2)\epsilon$ and termination errors into the F(k) of Fig. 1 and analyzing the result just as if it were experimental data with an unknown G(r). The residual errors, ΔF and ΔG , which are shown in Figs. 2(c) and 3(d), are negligible.

It should be noted that two additional types of errors, not considered above, may be of consequence under certain conditions. Instrumental broadening and the combined presence of $K\alpha_1$ and $K\alpha_2$ radiations can both

⁵ R. Kaplow (to be published).

cause a damping of the derived distribution function. These errors can be readily corrected if necessary, but are not significant in these experiments.

The data reductions were started in each case with dispersion-corrected⁶ Thomas-Fermi-Dirac theoretical values for the scattering factors.^{7,8} The precise values used in the initial reduction are not critical because of the error analysis discussed in the previous section. For our present purposes it is not necessary to know the source of the errors which were encountered and corrected in the analysis, but it is interesting to note that, apart from termination effects, the principal errors could be ascribed to uncertainties in the scattering factors.⁹ It is not possible to be certain, with experimental data, that all errors have in fact been removed, but the magnitude of remaining oscillations at small values of rand the value of ρ_0 in the final G(r) may be used as measures of the over-all efficacy of the procedure. These criteria have been well satisfied in the data presented here

In the final results, oscillations remaining at low values of r were slight or absent and the deviations in ρ_0 from values calculated from other data 10,11 were 6 and



FIG. 5. Intensity functions, F(k), for liquid lead and liquid mercury.

Publishing Company, Cleveland, Ohio 1957).



FIG. 6. Radial density functions for solid and liquid lead near the melting temperature compared with damped and broadened solid function.

1%, respectively, for low- and high-temperature lead and 3% for mercury.

IV. DISCUSSION OF RESULTS

The final corrected intensity functions F(k) for liquid lead at 329 and 600°C and liquid mercury at 25°C are shown in Fig. 5. The two curves for liquid lead are very similar, despite the rather large difference in temperature. The final distribution results are shown in terms of reduced radial density functions, $H(r) = 4\pi r^2 (\rho - \rho_0)$, in Figs. 6(a), 7, and 8. Numerical values for the maxima and minima of the oscillations in both F(k) and H(r) are given in Table I. The F(k) data for mercury are close to the results obtained by Pfannenschmid¹² but differ from

⁶ H. Templeton, Acta Cryst. 8, 841 (1955). ⁷ L. H. Thomas and K. Umeda, J. Chem. Phys. 26, 239 (1957). ⁸ International Tables for X-ray Crystallography, (Kynoch Press, Birmingham 1962), Vol. III.

⁹ R. Kaplow, S. L. Strong, and B. L. Averbach,"Acta Cryst.

⁽to be published). ¹⁰ Metals Handbook, edited by Taylor Lyman (American Society Metals, Cleveland, Ohio, 1961) Vol. I. ¹¹ Handbook of Chemistry and Physics (Chemical Rubber ¹¹ Handbook of Chemistry and Physics (Chemical Rubber)

¹² O. Pfannenschmid, Z. Naturforsch. 15a, 603 (1960).

Hg	25°C	Pb 6	00°C	Pb	Max and min positions in F(k) (14) Pb 331°C		
k F(k)	r H(r)	k F(k)	r H(r)	k F(k)	r H(r)	k	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2.2 max 3.2 min 4.2 max 5.2 min 6.0 max 7.1 min 8.1 max	

TABLE I. Maxima and minima in intensity and density functions $F(k) = k(I/f^2-1)$, $H(r) = 4\pi r^2(\rho(r)-\rho_0)$.

that obtained by Kruh et al.,13 as read from their published figures. The positions of the oscillations in F(k) for the low-temperature lead experiment are in good agreement with those tabulated by Sharrah et al.,14 which are reproduced in the table. Values and positions for the first peak in the total density function, $4\pi r^2 \rho(r)$, are given in Table II, where they are compared with previous results.14,15

The radial-density functions are convenient descriptions of the liquid structure, since they reflect the atomic distribution more directly than the distribution functions G(r). A common application of such data involves



FIG. 7. Radial density function for liquid lead at 600°C compared with damped and broadened solid function.

¹³ R. F. Kruh, G. T. Clayton, C. Head, and G. Sandlin, Phys. Rev. 129, 1479 (1963).
¹⁴ P. C. Sharrah, J. I. Petz, and R. F. Kruh, J. Chem. Phys. 32, 241 (1960).
¹⁵ P. C. Sharrah and G. P. Smith, J. Chem. Phys. 21, 228 (1953).

TABLE II. First peak in total density, $4\pi r^2 \rho(r)$.

Mercury									
Reference r $4\pi r^2 \rho(r)$	(This work) 3.03 14.80	(12) 3.03 15.0ª	(13) 3.05 14.5 ^a						
		Lead	ł						
$\begin{array}{c} \text{Tem-}\\ \text{perature}\\ (\text{Reference})\\ \textbf{r}\\ 4\pi r^2 \rho(r) \end{array}$	329° (This work) 3.39 12.60	600° (This work) 3.36 11.10	350° (15) 3.40 12.0ª	550° (15) 3.40 11.1ª	331° (14) 3.39				

* Estimated from published figures.

the evaluation of the quantity,

$$C_{i} = \int_{r_{i}-\Delta}^{r_{i}+\Delta} 4\pi r^{2}\rho dr, \qquad (8)$$

in the vicinity of each of the peaks, thus obtaining the number of first, second, third, etc. neighbors about a given atom. This procedure is uncertain here because of the overlapping of the peaks. The functions H(r), however, contain a considerable amount of structural information and, since we believe that our method of analysis has provided density functions with a reasonably true shape, we shall attempt to interpret the form of the curve for each liquid. This analysis is approached by obtaining radial density functions for random polycrystals of the corresponding solid at temperatures close to the melting point. The shapes of these functions for the solid are adequately described in terms of a crystal structure, a mean nearest neighbor distance r_1 , a mean square thermal displacement σ^2 , and coupling coefficients γ_i , which indicate whether the atomic vibrations in the *i*th shell are independent of those of the atom at the origin.¹⁶ In this section we show that the

¹⁶ R. Kaplow, B. L. Averbach, and S. Strong, J. Phys. Chem. Solids 24, 1195 (1964).



FIG. 8. Radial density function for liquid mercury at 25°C compared with damped and broadened solid function.

structure of each liquid may be described reasonably well in terms of modifications of the corresponding crystalline structure, whereas the structures of liquid lead and liquid mercury do not appear to be directly related.

A. Lattice Parameter and Average Density

A comparison of crystalline lead just below the melting point¹⁶ and the liquid just above shows that the major oscillations in the solid radial distribution tend to occur at slightly larger distances than corresponding oscillations in the liquid. The deviations are best seen at large radial distances (between 12 and 20 Å) where a decrease in the lattice parameter of 1.5% brings the solid into best agreement with the liquid. The radialdensity function of solid lead at 325°C is shown in Fig. 6(b) with the radial distance rescaled to correspond to a lattice parameter 1.5% smaller than the experimental solid value. (It should be noted that the ordinate scale for the solid function differs from that of the liquid for convenience in plotting.) The rescaling of the radial distance also brings the first peak in solid and liquid lead to virtually the same position. If we assume that the structure of the liquid can be described in terms of the solid, the specification of an apparent lattice parameter which fits the liquid oscillations best (particularly at large values of r) is equivalent to the specification of an apparent mean nearest neighbor distance. This distance need not correspond exactly to a maximum in the distribution function. The apparent mean first neighbor distance r_1 in liquid lead is thus 1.5% smaller than in the solid at the melting temperature. This value remains unchanged in raising the liquid to 600°C. This reduction is approximately equivalent to the total lattice expansion up to the melting point, and it appears that the crystal structure prevents the lead atoms in the solid from achieving the closest possible nearest-neighbor distance.

Using the first-neighbor distance r_1 for the liquid, it is possible to compute a "close-packed" lattice density, 0.0333 atoms/Å³. This value may be compared with the densities of 0.0309 and 0.0298 atoms/Å³ obtained when the solid density is adjusted by the experimental change in density on melting and by the expansion on heating to 600°C.¹⁰ The differences indicate that liquid lead has an excess volume of 7.3% at 329°C and 10.4% at 600°C. Liquid mercury compared in the same way to the corresponding rhombohedral structure has an excess of 3% at 25°C. These values of excess volume become the percentages of vacancies if we assume that each vacant site has the same volume as the corresponding atom. The ratio of the excess volumes in liquid lead at 600 and 320°C is 1.43, and this is also the ratio between the two temperatures, suggesting that the excess volume, or vacancy concentration is proportional to the temperature. Although the nearest-neighbors in liquid lead are closer than in the solid, the number of atoms at most radial distances in the liquid is smaller. Since r_1 does not change as the temperature is raised, the expansion of the liquid may be associated entirely with an increase in the excess volume.

B. Critical Correlation Distance

A comparison of the liquid radial-density function for lead in Fig. 6(a) with that of the corresponding solid in Fig. 6(b) shows two principal differences: (1) the peaks in the liquid curve are strongly damped as r is increased; (2) the liquid peaks beyond the first are broadened more than in the solid. From the nature of the resultant transformations we assume that the damping arises primarily from a consistent loss of correlation at radial distances greater than some critical value, and the broadening is associated principally with atomic motions which may be a combination of vibrational and diffusive displacements. These effects are treated separately, and we shall first consider the critical correlation distance. The existence of a critical correlation length is analogous to the assumption of a small particle size in a crystalline material. However, we do not imply that physical boundaries cause this loss of correlation in the liquid, and this effect is probably a consequence of the large atomic displacements. For the time being, however, it is convenient to describe the liquid in terms of a critical correlation distance d and mean square relative displacements σ^2 , since these quantities may be derived from the experimental functions H(r). We assume nearly spherical perfect domains of diameter d which fill all space, but which are randomly oriented with respect to one another. The radial density



FIG. 9. Damping function arising from critical correlation distance d.

function for a domain of infinite size is H(r). A spherical shell of radius r < d, centered inside a particular domain will lie partially inside the domain, where the density function is H(r), and partially outside, where the density function is zero. An average over all possible origins inside the domain gives the modified density at r, $H^*(r)$. The ratio, $H^*(r)/H(r)$, is shown in Fig. 9 as a function of the reduced radius r/d. Although both the broadening and damping factors were adjusted to give the best fit with the experimental liquid pattern, it is interesting to observe the effect of the damping alone. Figure 6(c) is the result of damping the solid function given in 6(b), using the final value, d=22.4 Å, and it is evident that the resultant damped function has many features of the liquid. The final value for lead at 600°C was d = 20.0 Å, and d = 40 Å for mercury at 25°C.

C. Atomic Displacements

We may consider two types of atomic motion. The atoms may oscillate about a mean radial distance in analogy with the thermal vibration of an atom about a lattice point. This is consistent with the ability of a liquid to transmit longitudinal elastic waves. However, there is also a rapid diffusive motion, as indicated by the high values for the self-diffusion coefficients. In the case of liquids, both types of motion have similar characteristics; the atomic displacements at large distances are independent of the correlation distance r whereas at smaller distances the motions of neighboring atoms are coupled. Since the x-ray experiment averages over both time and over the irradiated volume of the specimen, the correlation probability for an atomic shell of radial separation, r_i , will be broadened by a mean-square thermal displacement σ_t^2 and a mean-square diffusive displacement σ_{d^2} . The diffusive displacement σ_{d^2} is not important in the solid correlation function, because the number of atoms undertaking a diffusive jump is much smaller than in the liquid. The x-ray experiment averages the diffusive excursions of atoms in the same way as it averages the thermal vibrations, and it is thus impossible to separate these two motions in the liquid without additional assumptions.

We define a mean-square total displacement $\sigma^2 = \sigma_i^2 + \sigma_d^2$, which includes both types of motion, and a series of coupling coefficients q_i where $q_i = \sigma_i^2 / \sigma_{\infty}^2$ for the *i*th

shell, and σ_{∞}^2 is the mean-square displacement for an infinite separation of the atoms. The meaning of the coupling factors may be seen by considering only vibrational displacements. Let u^2 be the total meansquare vibrational displacement of an atom from a definite site. If the vibrations are isotropic, the meansquare displacement along any direction, u_s^2 , is $u^2/3$. If two atoms, separated by r_i , vibrate independently, the mean-square relative displacement σ_i^2 along the vector between them is $2u_s^2$. If the atoms vibrate completely in harmony, however, then $\sigma_i^2 = 0$ regardless of u_s^2 ; that is, $q_i = 0$. If the atoms tend to vibrate in phase, $0 < q_i < 1$, while if they tend to vibrate out of phase, $1 < q_i < 2$. The definition of σ^2 for the liquid, as the sum of σ_t^2 and σ_d^2 , implies that the two types of displacements are independent.

Using the solid structure as a basis, each atomic shell is replaced by the function,

$$B(r-r_i) = \frac{C_i}{(2\pi q_i \sigma_{\infty}^2)^{1/2}} \exp\left[\frac{(r-r_i)^2}{2q_i \sigma_{\infty}^2}\right], \quad (9)$$

where C_i is the number of atoms in the *i*th shell. A Gaussian broadening has been assumed in Eq. (9), but it is evident that this form can only be an approximation. The relative atomic motions at small values of rare markedly asymmetric. However, neglecting this asymmetry for the moment, if we assume that the coupling factors vary in a continuous fashion with radial separation, it is possible to obtain a fit with the observed liquid functions. We start with the relative shell positions and occupation numbers of the crystal structure, choose the nearest-neighbor distance which gives a best fit to all the oscillations in the liquid structure, broaden the shells with the expression given in Eq. (9), damp the resultant function with the factors shown in Fig. 9, and adjust the scale to account for the actual liquid density. By varying the values of nearest neighbor distance r_1 , the critical correlation distance d, the mean square displacement σ^2 , and the coupling coefficients q_i , it has been possible to obtain a unique best fit to the experimental result. It should be stressed that r_1 is not necessarily the exact position of the first-peak maximum in G(r), but is the value derived from the structure lattice parameter which gives the best fit to the experimental distribution function.

The liquid parameters are summarized in Table III. The resultant fit may be seen in Figures 6, 7, and 8, where we compare the experimental liquid-density function with the one obtained by performing these transformations on the corresponding solid structure. The positions of the oscillations match well, and the fit is nearly perfect over much of the function. The fit is poorest in the region just beyond the first shell, where the assumption of a symmetric atomic displacement function is known to be poor. This and other differences can probably be accounted for by a more exact diffusive broadening function. It should be noted that we were

			$\begin{array}{cccc} r_1 & d & \rho_0 & \sigma^2 \\ \begin{pmatrix} \lambda \\ \end{pmatrix} & \begin{pmatrix} \lambda \\ \end{pmatrix} & otomy \begin{pmatrix} \lambda \\ \lambda \\ \end{pmatrix} & \begin{pmatrix} \lambda \\ \lambda \\ \end{pmatrix} \end{array}$				σ_{t^2}	σ_d^2	Δρ excess	$\Delta \rho$ excess		Coupling factors for σ^2 shell						
Lead (fcc)	solid: liquid: liquid:	325°C 329°C 600°C	3.54 3.49 3.49	22.4 20.0	0.0317 0.0309 0.0298	0.175 0.28 0.33	0.175 0.175 0.175	0.105 0.155	7.3% 10.4%	0.47 0.32 0.32	0.59 0.50 0.50	0.68 0.70 0.70	0.76 0.80 0.80	0.81 0.90 0.90	0.86 1.0 1.0	0.92 1.0 1.0	0.95 1.0 1.0}	16 this work
Mercury (Rhombohedral)	solid: liquid:	-46°C 25°C	split shell 3.00– 3.46 3.03	∞ 40.0	0.0431 0.0407	 0.70	····	••••	 3.0%		 0.20	 0.40	 0.30	 0.50	 0.80	 0.90	 1.0	this work

TABLE III. Structure parameters.

unable to start with the fcc Pb structure and fit the liquid Hg pattern. Conversely, we were unable to start with the rhombohedral Hg pattern and fit the liquid Pb structure.

Even though the liquid and solid structures appear to be uniquely related, it is not certain that the vibrational and diffusive motions are separable. We may consider the feasibility of such a separation by comparing the total density function $4\pi r^2 \rho$, in the vicinity of the nearest neighbor region. The width of the first peak, on the small r side, should be determined primarily by the mean vibrational amplitude. Figure 10 shows that the maximum in the first neighbor peak for liquid lead at 329°C is 0.10 Å closer to the origin than the solid peak, and the maximum for the liquid at 600°C is about 0.13 Å closer.

The extent of the radial shift appears to be proportional to the excess volume in the liquid, and the most probable separation appears to increase as the number of neighbors increases. If we consider the halfwidth at half-maximum, measuring from the peak position to the left side of the curve, we obtain 0.31 Å for the solid at 325°C, 0.29 Å for the liquid at 329°C, and 0.28 Å for the liquid at 600°C. The mean and most



FIG. 10. Total radial density function for Pb in vicinity of nearest-neighbor distance.

probable positions do not coincide even in the solid,¹⁶ but if we use the mean positions r_1 , we also find that the widths are substantially the same. We thus conclude that the vibrational motion at both temperatures in the liquid is substantially the same as in the solid. This also implies that the nearest-neighbor coupling factors for the thermal motion are also retained in the liquid.

The total mean atomic displacements, $\sigma^2 = q_i \sigma_{\infty}^2$, for the solid as well as the liquids, are shown in Figs. 11 and 12. At large distances, the coupling coefficients, q_i , must approach unity and the displacement becomes σ_{∞}^2 . The coupling coefficients for the liquid structures approach unity at about 12 Å. The coupling coefficients for solid lead approach unity at about 20 Å. If we assume that the thermal motion for the liquid is that of the solid at the melting temperature, the difference between the solid and the liquid curves gives the mean square diffusive displacements, σ_d^2 . These are shown in Fig. 13. It should be noted that coupling factors less than unity for the diffusive motion are observed at low values of r, and values which are apparently greater than unity at intermediate distances of about 12 Å. It may be, however, that the low values at low r are due in part to the Gaussian assumption, and that the high q region is an artifact due to a more rapid loss of vibrational correlation in the liquid than the solid.

We now assume that the excess volume in the liquid consists of vacancies and use the crystalline random walk model for self-diffusion. The diffusion coefficient



FIG. 11. Total mean-square atomic displacements in lead.

may be written as

$$D = (C_1/6)r_1^2 f_{v}\nu \exp(-(Q/kT)), \qquad (10)$$

where r_1 is the nearest-neighbor distance, C_1 the number of nearest neighbors, f_v the fraction of vacancies, v the mean vibrational frequency, and Q the activation energy for motion. It has already been mentioned that f_v appears to be proportional to the absolute temperature. If we insert that relationship, $f_v = 1.2 \times 10^{-4}T$, the mean frequency calculated from the Debye temperature of the solid, 69°K, $r_1=3.5$ Å and $C_1=12$, the equation for the diffusivity of liquid lead contains only one free parameter Q and

$$D = 3.2 \times 10^{-7} T \exp(-Q/kT).$$
(11)

Taking the value $D=2.5\times10^{-5}$ cm²/sec¹⁷ at T=600 °K, Q is calculated to be 0.10 eV. The fit to the available diffusion coefficient data is good. Walls and Upthegrove¹⁸ have previously suggested an identical form for the temperature dependence and have shown that virtually all liquid diffusion coefficient data can be described by such an expression.

V. SUMMARY

We have presented a method of analysis which appears to eliminate the spurious detail from experi-



FIG. 12. Total mean-square atomic displacements in mercury.



FIG. 13. Mean-square diffusive displacements in liquid lead.

mentally derived radial-density functions. In attempting to describe the resultant liquid-density functions for liquid lead and liquid mercury, the following conclusions may be drawn:

1. There is a close correspondence between the liquid and the corresponding polycrystalline solid structure. On the other hand, there does not appear to be a common liquid structure which will describe the radial density functions of both liquids.

2. If we start with the radial-density function of the solid, we can describe the resultant liquid-density function by means of the following additional parameters: r_1 =mean nearest-neighbor distance, ρ_0 =average density of the liquid, d=critical correlation distance, σ_{∞}^2 = total mean square relative atomic displacement at infinite separation, q_i =coupling coefficients for the atomic displacements.

The crystalline lattice is thus used as a framework for describing the liquid. The separation of the atomic displacements into thermal and diffusive components is less certain, but the shape of the density function at the nearest-neighbor distance suggests that the thermal vibrations of the liquid are the same as those in the solid at the melting point.

ACKNOWLEDGMENTS

The authors would like to acknowledge the sponsorship of the U. S. Office of Naval Research and their continued interest in these liquid-structure studies. The assistance of the MIT Computation Center is also gratefully acknowledged.

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 ¹⁸ H. A. Walls and W. R. Upthegrove, Acta Met. 12, 461 (1964).