

# THE PHYSICAL REVIEW

*A journal of experimental and theoretical physics established by E. L. Nichols in 1893*

SECOND SERIES, VOL. 129, No. 4

15 FEBRUARY 1963

## Structure of Liquid Mercury\*

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(Received 5 October 1962)

Because the only available studies of the temperature dependence of liquid mercury's x-ray scattering contain false peaks in the intensity, a re-examination has been made over a  $60^\circ$  range ( $-36^\circ$  to  $26^\circ$ ) under precisely reproducible geometry. The fact that there is little variation in observed intensity and in the derived radial distribution function is consistent with the small density decrease (1%) over the range, and with the idea that scattering from hard spheres depends only upon density. The mean number of nearest neighbors is 7.5 centered at 3.03 Å.

THE only available studies<sup>1</sup> of the temperature dependence of liquid mercury's x-ray scattering contain false peaks in the recorded intensity. Although a number of subsequent experiments<sup>2</sup> have demonstrated these flaws, none has been carried out over a range of temperature. Because of this, we felt that it would be desirable to re-examine the temperature dependence of mercury's x-ray scattering.

In order to make meaningful comparisons, measurements over identical angular ranges were made in the precisely reproducible geometry afforded by a special diffractometer described earlier.<sup>3</sup> Intensity measurements (Fig. 1) were made from just above the melting point ( $-38.9^\circ\text{C}$ ) to room temperature with x radiation of wavelength 0.709 Å.

The intensity curves are practically identical with the exception of a small shoulder on the first peak which disappears at higher temperature. Although significant broadening of peaks with increasing temperature has been observed for inert gases,<sup>4</sup> this effect is mostly due

to large density decreases. In this work, the molar volume changes by only about  $0.2\text{ cm}^3$  or 1%, and much higher temperatures would be needed to produce noticeable broadening.

The radial distribution functions (RDF's) in Fig. 2 are, therefore, quite similar and show major maxima at 3.03 and 6.00 Å. Although the first maximum seems narrower at  $-36^\circ$ , the area under the first maximum remains constant for each curve. The mean number of nearest neighbors is about 7.5 as compared to 6 at 3.00 Å in the crystal. The small differences in the several curves are in the artificial detail produced by slight variations in the intensity curves, each of which is fitted to the same independent scattering.

Part of the small detail consists of a ripple extending over the entire RDF. Since it is likely that the small maxima result from the termination of data taking at a finite value of the scattering parameter,  $s=4\pi\lambda^{-1}\sin\theta$ , two tests were made to establish that termination is the origin of the small peaks. First, a damping factor  $\exp(-as^2)$  was applied to one of the intensity curves inasmuch as this has been shown to diminish the effect of termination.<sup>5</sup> The suppression of the ripple in the resulting RDF is shown in Fig. 2. Second, a series of RDF's was calculated from one of the intensity functions with the Fourier integral arbitrarily terminated at successively decreasing values of the scattering parameter. The series is shown in Fig. 3, and the shift in the positions of subsidiary maxima agrees with that

\* The support of the United States Atomic Energy Commission is gratefully acknowledged.

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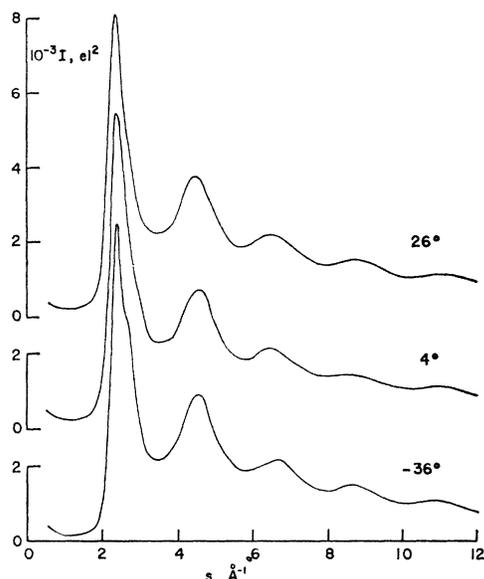


FIG. 1. Intensity data for liquid mercury.

expected to arise from termination.<sup>5</sup> We conclude that only the major peaks are descriptive of the liquid at this resolving power.

The series in Fig. 3 demonstrates that termination has an effect on the location of maxima in the RDF, and that this is a general effect which should be considered in comparing different investigations and in deducing the characteristics of pair potential functions

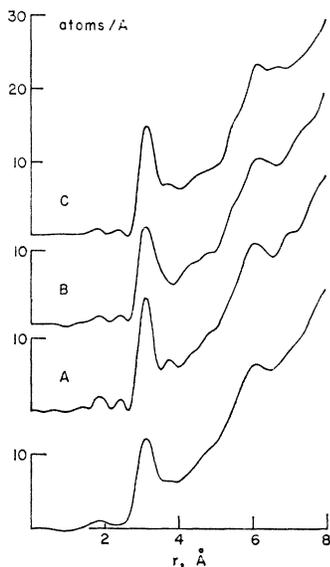


FIG. 2. Radial distribution functions for liquid mercury. Curves A, B, C are for  $-36$ ,  $4$ , and  $26^\circ\text{C}$ , respectively. The unlabeled lower curve is obtained by including a damping factor  $\exp(-0.01s^2)$  in the Fourier integral for  $-36^\circ\text{C}$ .

from RDF's. The diffraction data yield directly the differential density function,  $4\pi r^2(\rho - \rho_0)$ , the maxima in which are broadened and shifted to larger  $r$  the smaller the cutoff value of  $s$ . When a peak at a given value of  $r$  in the differential density is added to the parabola  $4\pi r^2\rho_0$  to give the RDF, the maximum in the RDF occurs at a larger  $r$  value the broader the peak in the differential density. Both of these effects combine to produce shifts as big as  $0.3 \text{ \AA}$ , and this is apparent in Fig. 3, except for Curve A.

The present study shows little detectable changes in the structure of liquid mercury over a  $60^\circ$  range of temperature. The first two concentrations of nearest neighbors lie at distances whose ratio (approximately 2:1) is greater than that predicted for the random close packing of equal spheres (1.8:1).<sup>6</sup> Moreover, the mean

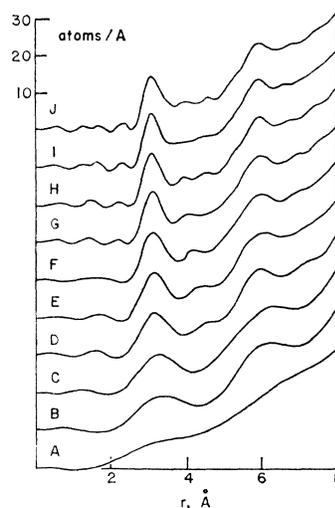


FIG. 3. The effect of termination of the Fourier integral upon the radial distribution function. Curves A through J were obtained by terminating the Fourier integral at  $s$  values of  $2.4$ ,  $3.1$ ,  $4.2$ ,  $5.2$ ,  $6.3$ ,  $7.3$ ,  $8.7$ ,  $9.4$ ,  $10.8$ , and  $12.0 \text{ \AA}^{-1}$ , respectively. These  $s$  values are the ones at which the Fourier integrand  $s(I - f^2)/f^2$  equals zero.

number of nearest neighbors is less than that expected for the random arrangement (namely, 8.5).<sup>6</sup> These two factors combine to give liquid mercury a much lower density than nearby lead and gold. The nature of the forces responsible for this is unknown. The proposed<sup>7</sup> retention of the crystalline arrangement of nearest and next nearest neighbors is not supported by the available RDF's. The small maximum to the right of the first maximum had suggested this,<sup>7</sup> but this maximum is shown to arise from termination. Retention of crystalline arrangement would require two approximately equal peaks (6 atoms) at about  $3.0$  and  $3.5 \text{ \AA}$  in the RDF.

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<sup>7</sup> J. S. Lukesh, W. H. Howland, L. F. Epstein, and M. D. Powers, *J. Chem. Phys.* **23**, 1923 (1955).