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W. E. MORRELL AND J. H. HILDEBRAND, *Department of Chemistry, University of California*

(Received January 3, 1936)

A three-dimensional model molecular assemblage has been constructed permitting a determination of the relative frequency of occurrence of the varying intermolecular distances. The model simulates the expansive effect of temperature. A good approximation is obtained to the distribution of molecules in liquid mercury determined by Menke by the aid of x-ray diffraction.

THE number of molecules of a pure fluid in a spherical shell of radius r and thickness dr is (N/v) $4\pi r^2 dr$ (where N is Avogadro's number and v is the molal volume), provided r is large. When r becomes small, however, a function of r, which has been designated by W, must be introduced, because the positions of the molecules in the shell are influenced by the positions of their neighbors. The number of molecules in the shell is then (N/v) $4\pi W r^2 dr$. We may define W as the average number of molecules per unit volume (v/N) at distance r from a central molecule.

The determination of this distribution function, W, would permit important conclusions to be drawn regarding intermolecular forces and such related problems as solubilities.[1] Its purely mathematical analysis, in the case of rather condensed systems, where the molecular field surrounding each molecule must be approximately constant, offers attractive possibilities complicated by difficulties which have thus far not been surmounted. Probably the most successful mathematical treatment to date is that of Kirkwood,[2] who, by statistical-mechanical methods, obtained a complicated "approximate molecular pair distribution function, typical of dense fluids." Experimental determination of the distribution function by the aid of x-ray diffraction has been carried out in the cases of mercury and liquid gallium by Menke,[3] and at two different temperatures for water by Katzoff.[4] Menke's distribution function for mercury is reproduced in Fig. 2A. Kirkwood's curve only roughly approximates this experimental curve.

Another type of investigation which throws light upon the variation of W with r is the use of models and direct measurement. Thus Menke,[3] by merely pouring steel spheres onto a flat surface and measuring each time the distance between two black ones, then tabulating these distances, obtained a curve for two dimensions which had the characteristics of his W curve for mercury. Very similarly, Prins[5] poured seeds onto a glass plate and photographed them. He then drew concentric circles on the negatives around "central" seeds, counted the numbers between circles, and obtained the two-dimensional "W" for this case, or the number per unit area at various distances from the central seed. Here also, curves were obtained which at least roughly resemble the distribution function for mercury.

The present work is an extension of this use of models, under conditions, however, which should more nearly duplicate those in an actual liquid. We have used three dimensions instead of two, practically neutralized the force of gravity on the individual particles, put the "molecules" in motion, and have taken more measurements and at smaller intervals.

The model "molecules" were gelatin spheres. These spheres were made by allowing drops of a hot gelatin solution (15 grams per 100 cc of water) to fall into a column of "crystal" oil surrounded by an ice bath, the gelatin becoming hard before the spheres reached the bottom of the column. A few black spheres were made by mixing lamp black into part of the hot gelatin. The oil was washed from the balls with ether, then the ether washed away with water.

An environment for the spheres was made by heating part of the clear gelatin solution over a

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[1] J. H. Hildebrand and S. E. Wood, J. Chem. Phys. **1**, 817 (1933).

[2] J. G. Kirkwood, J. Chem. Phys. **3**, 300 (1935).

[3] H. Menke, Physik. Zeits. **33**, 593 (1932).

[4] S. Katzoff, J. Chem. Phys. **2**, 841 (1934).

[5] J. A. Prins, Naturwiss. **19**, 435 (1931).

water-bath for some 12–16 hours—until it no longer solidified when cooled. This solution retains practically the same density and refractive index as the spheres, or can be adjusted to these conditions by the addition of a little water. The solid balls, then, when placed in this solution would neither sink nor rise to the surface and were practically invisible. On the other hand, the few black spheres put into the mixture were clearly and sharply defined.

The solution and spheres were placed in a small plate-glass cell. Shadow pictures of the mixture were made by means of a mercury spark. A small metal frame clamped the film firmly against two sides of the box, and by use of a mirror each exposure was made simultaneously from two directions at right angles. Before each exposure, while a new film was being placed in the frame, the cell was tipped in various directions and shaken somewhat, then as quickly as the cell was in position and before the motion of the spheres had completely ceased, the picture was snapped.

One of the resulting photographs is shown in Fig. 1.

The black spheres on the negatives were numbered consecutively from top to bottom for the sake of convenience in recording their positions. Their distances from the axes at the right and bottom of each half of the film, scratched on the walls of the glass cell, were measured by the aid of a vernier caliper. Given the X, Y, and Z positions of each black sphere, the values for ΔX, ΔY, and ΔZ for each possible pair were obtained merely by subtractions. The distance, r, between each pair was given by $r = (\Delta X^2 + \Delta Y^2 + \Delta Z^2)^{\frac{1}{2}}$. We found that the thousands of repetitions of this problem were most conveniently handled on a slide rule with an appropriate square and square root scale.

The distances between all possible pairs of black spheres having been thus calculated from a series of photographs, the number of times that each distance occurred was tabulated. If this number be x, the total number of measurements obtained from the series can be designated $\sum_{0}^{\infty}x$. Then $x/\sum_{0}^{\infty}x$ is the relative frequency with which this particular distance occurred in the series, or it is the relative chance that a
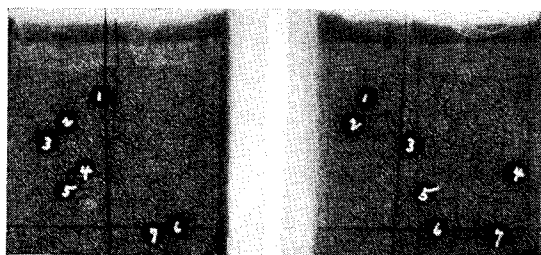
particular black sphere would at a certain time be found at a given distance r from a particular ball arbitrarily chosen as the central one. Since there are N spheres in the box, the chance that any of them, no matter which, would at that time be at distance r from the central one is $(N-1)x/\sum_{0}^{\infty}x$, or this is the probable number of balls which at any time would be found at distance r from the central one. The number which would probably be found within a spherical shell of inner radius r_1 and outer radius r_2 is $(N-1)\sum_{r_1}^{r_2}x/\sum_{0}^{\infty}x$. The number per cc within this shell would be

$$(N-1)\sum_{r_1}^{r_2}x/\sum_{0}^{\infty}x \int_{r_1}^{r_2} 4\pi r^2 dr.$$

Hence the number of spheres per unit volume at distance r from the central sphere would be

$$V(N-1)\sum_{r_1}^{r_2}x/N\sum_{0}^{\infty}x \int_{r_1}^{r_2} 4\pi r^2 dr,$$

and this by definition is W. Integrating, the expression becomes:

$$W = 3V(N-1)\sum_{r_1}^{r_2}x/4\pi N\sum_{0}^{\infty}x(r_2{}^3 - r_1{}^3). \quad (1)$$

By means of this equation and the data obtained from the photographs, the value of W at each value of r was calculated. The results of four series of measurements are plotted in Fig. 2B, C, and D.

In these figures the points represented by the solid dots were obtained by taking $r_2 - r_1 = 0.05$ cm, and the circles by using $r_2 - r_1 = 0.09$ cm. The points on D were determined only with $r_2 - r_1 = 0.05$ cm. The values of the various constant quantities occurring in Eq. (1), to-

TABLE I.

SERIES	TOTAL NO. MEAS-URE-MENTS (Σx)	TOTAL NO. SPHERES (N)	NO. BLACK SPHERES	DIAMETER OF SPHERES	VOLUME OF "SYSTEM" (V)	"EXPAN-SION"
B	1121	614	7	0.422 cm	60 cc	1.84
B'	820	300	6	0.48 cm	45 cc	1.92
C	1120	371	7	0.432 cm	60 cc	2.84
D	1035	500	10	0.39 cm	30.5 cc	1.45

gether with other information concerning each series, are summarized in Table I.

The "expansion" is the ratio of the total volume of the mixture to that which would be occupied by the balls, together with the space between them, if they were allowed to settle into a completely regular, closest-packed arrangement. In other words, it is the ratio of V to 0.707 D^3N, where D is the diameter of the spheres.

The "expansions" of two of the series, B and B', were practically equal, hence they were plotted together in B.

It will be noted that the less "expanded" the mixture, the higher and sharper is the first maximum. This is exactly what should be expected, and agrees also with the results of Prins.[5] The extreme case would be a regular, close-packed arrangement, either hexagonal close packing or cubic close packing. In these cases the distribution functions become discontinuous. These are given for comparison in Fig. 2E.

These varying "expansions" were introduced to simulate the effect of temperature. As a sample of the degree of expansion of an ordinary liquid we may cite carbon disulfide, whose volume at 25°C is 1.25 times its volume extrapolated to absolute zero.

A curve showing these close-packing effects more markedly was obtained in our preliminary measurements. In this case glass spheres were used instead of gelatin, a few being colored with water paints. They were immersed in a solution of bromoform and carbon tetrachloride, the mixture being so adjusted as to have the same refractive index as the glass. However, the spheres were denser than the liquid, hence sank to approximately close-packed, though jumbled, arrangements. The positions of the colored ones were read directly, instead of being measured

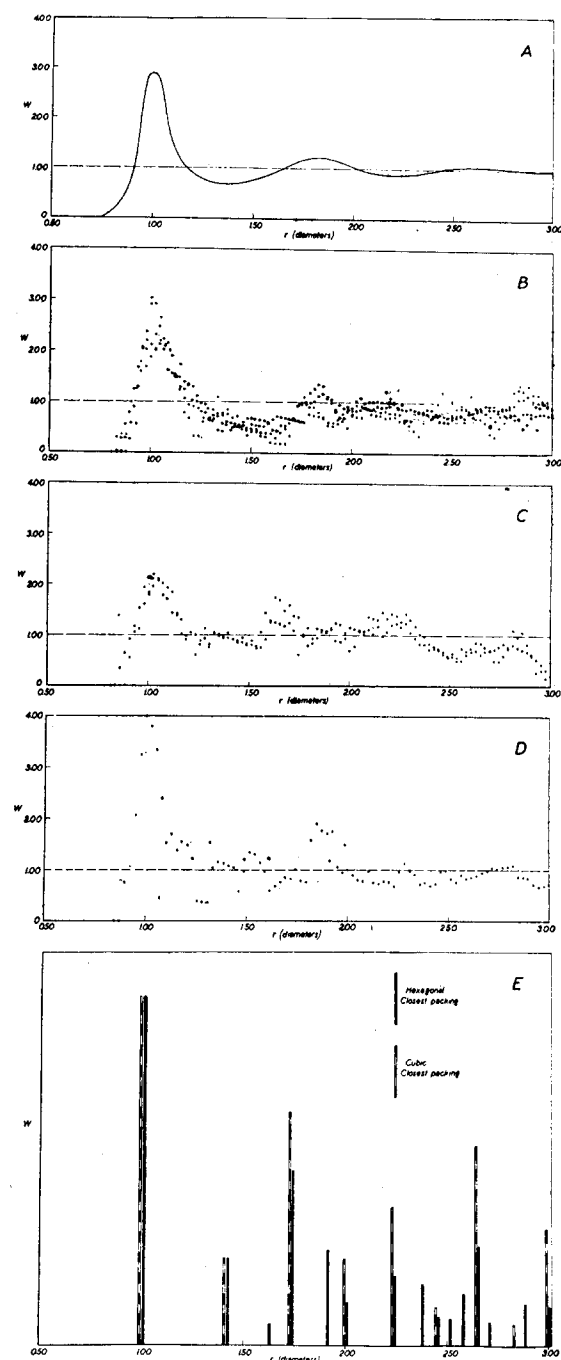from photographs. (This method of measurement was also used in D.)

FIG. 2. A, Menke's[3] distribution function for mercury; B, two distribution functions, superimposed, obtained with gelatin spheres, "expansions" 1.84 and 1.92; C, "expansion" 2.84; D, "expansion" 1.45; E, discontinuous distribution functions for regular close-packed arrangements.

In opposition to close-packed arrangements, very high "expansions," or a gas-like structure, should give distribution functions with a very low first maximum or no peak at all, and practically no fluctuations from unity at distances greater than one diameter.

Because of the smallness to the cell used in these experiments, the values of W tend to sag below the unity line at the larger distances, since these larger distances could not occur relatively as frequently as they would in a box of infinite size. This effect, within the region considered, could have been practically eliminated by the use of a larger container. This, however, would have greatly increased the number of observations necessary to supply the same number of measurements at the shorter distances, and it is at these smaller distances that the determination of the distribution function is of most value. Beyond a couple of diameters the function fluctuates little from unity, as Menke's curve shows. Within a couple of diameters this sagging effect plays very little part, so the added labor incident to the use of a larger cell was not considered worth while.

Thus by the use of a model molecular assemblage we have been able to duplicate the principal characteristics of the molecular distribution function obtained for mercury. Presumably the atoms in liquid mercury are distributed much as are the spheres in these model liquids. This distribution, while practically random with respect to a central molecule at distances greater than a couple of diameters, is far from random at smaller distances. Within these shorter distances the distribution shows remnants of a regular, close-packed, or crystalline structure.

It might be noted in this respect that Kratky,[6] from a study of Menke's curve for mercury and comparison with curves which he calculated from assumptions of various possible types of packing, concludes that the residual ordered arrangement in liquid mercury is of the hexagonal close-packed type. Probably a better conclusion would be that it is a mixture of both hexagonal and cubic packings, which are represented by Fig. 2E. Thus glass spheres poured into a pile will pack cubically as often as hexagonally. If a layer of such spheres be arranged in hexagonal or honeycomb fashion, then a second layer on top of the first, then the first sphere of a third layer be added, it will be found that it can take either of two positions relative to the lower layers. Either it can be put directly above a sphere of the first layer or it can be placed on the continuation of a straight line joining the centers of a sphere of the first layer and an adjacent sphere in the second layer.[7] The first case gives hexagonal packing, the second, cubic, and there is no *a priori* reason why the one should occur in preference to the other. It seems likely that both types should occur in liquid mercury, especially since the thermal motions prevent a completely regular, close-packed arrangement. Indeed, an examination of Kratky's curves shows that an average of the two types would match Menke's curve for mercury better than does the hexagonally-packed curve alone.

It would be interesting and enlightening to extend the study of the distribution functions by means of model liquids to cases involving spheres of different sizes, and these at various "mole fractions." The method might also be extended to "molecules" of other forms, such as sausage-shaped, where orientation as well as distance would have to be considered.

A knowledge of these distribution functions for various types of liquids and solutions, and their variations with concentration and temperature, would permit a forward step in the study of the liquid state.

We wish to acknowledge certain suggestions for the construction of our model system made by Professor J. E. Gibson.

[6] O. Kratky, Physik. Zeits. **34**, 482 (1933).

[7] See W. H. Bragg and W. L. Bragg, *The Crystalline State* (G. Bell and Sons, London, 1924), p. 144.