[10] It is to be noted that n_2 in V corresponds to structure 2 and should not be confused with that corresponding to the vacancies only in V_2.

[11] R. Furth, Proc. Cambr. Phil. Soc. 37, 252 (1941).

[12] S. V. Lechter and R. T. Beyer, J. Acoust. Soc. Am. 35, 1571 (1963).

[13] J. Jarzynski and T. A. Litovitz, J. Acoust. Soc. Am. 41, 1290 (1964).

[14] R. Zwanzig and R. D. Mountain, J. Chem. Phys. 43, 4464 (1965).

[15] R. M. Waghorne, V. G. Rivlin, and G. I. Williams, Advan. Phys. 16, 215 (1967).

[16] H. Richter and G. Breitling, Advan. Phys. 16, 293 (1967).

[17] E. H. Carnevale and T. A. Litovitz, J. Acoust. Soc. Am. 27, 547 (1955).

[18] K. G. Plass, Acustica 13, 240 (1963).

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Measurement of the Coherent Neutron Scattering Amplitude of Deuterium, Mercury, and Fluorine by Mirror Reflection*

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The bound coherent neutron-scattering amplitudes of deuterium, mercury, and fluorine have been measured by the mirror-reflection method. The measured values are $a_D = +6.21 \pm 0.04$ F, $a_{Hg} = +12.67 \pm 0.13$ F, and $a_F = +5.83 \pm 0.17$ F. The mercury and fluorine values are in agreement with presently accepted values. The deuterium value departs seriously from most previously reported measurements. This value implies $+6.13 \pm 0.04$ F for the quartet scattering amplitude, $+0.13 \pm 0.05$ F for the doublet scattering amplitude, and 3.15 ± 0.04 b for the free-atom scattering cross section of deuterium.

INTRODUCTION

This paper describes measurements of the coherent neutron scattering amplitude of deuterium, fluorine, and mercury done by the mirror-reflection method of the Livermore Pool-Type Reactor. The theory of measurement of coherent neutron scattering amplitudes by reflection from mirror surfaces, as well as the experimental arrangement used in these measurements, has been described in the literature.[1-5]

METHOD OF MEASUREMENT

Our experimental procedure consists of finding the angles at which the reflected neutron intensities from a standard liquid and from a liquid containing the unknown element are the same. Since equal reflected intensities imply equal reflection coefficients, we have the relation

$$(\phi_1{}^2)^{-1}\sum_i N_i a_i = (\phi_2{}^2)^{-1}\sum_j N_j a_j \ , \qquad (1)$$

which does not depend explicitly on the spectral distribution of the incident neutron beam. The subscripts i and j in Eq. (1) refer to the constituents of mirrors 1 and 2 respectively; N and a stand for the number of scattering centers per unit volume and their coherent neutron scattering amplitudes; and the angles ϕ_1 and ϕ_2 are those yielding equal intensities from the corresponding mirrors. That is, in order to carry out the measurement, the angles of equal intensity, the chemical composition of both mirrors, and the coherent neutron scattering amplitude of all constituents but the one to be measured must be known.

Equation (1) is not valid, however, unless the reflected intensities are corrected for incoherence and absorption. Some knowledge of the incident neutron spectrum is required before these corrections can be made. The corrections applied to the experimentally determined intensities account for: (1) gain drifts in the detectors and amplifiers, (2) changes in the mirror density with temperature, (3) fast- and thermal-neutron backgrounds, (4) scattering of both incident and reflected beams in the vapor above the liquid surface, (5) variation of the incident beam intensity with angle, (6) finite angular divergence of the beam, and (7) incoherent scattering and absorption in the mirror. These corrections are described in detail in Ref. 3, pp. 535–538. Corrections (1) through (5) are simple and straightforward. Once they have been made, the reflected intensity is given by

$$I_{\exp}(\phi_0) = \int_{\phi_0-\Delta\phi}^{\phi_0+\Delta\phi}\Big[\int_0^{k_{\mathrm{Be}}} R(\phi, A, \gamma, k) \times \Phi(k)\, T(\phi) dk\Big] d\phi \qquad (2)$$

where

R is the reflection coefficient of the surface,

$A = \sum_j N_j a_j$ for the j constituents of the mirror,

$\gamma = \sum \{[N\sigma(k)]_{\mathrm{incoherent}}\}_j + \sum \{[N\sigma(k)]_{\mathrm{absorption}}\}_j$,

$\Phi(k)$ is the incident flux distribution (beryllium-filtered spectrum),

$T(\phi)$ is the triangular transmission function of the collimator,

$\Delta(\phi)$ is the angular divergence of the beam, and

k_{Be} is the beryllium cutoff wave number.

The beryllium-filtered-spectrum function $\Phi(k)$ is approximated by the following equations:

$$\Phi(k) = Ck^{a+b/k+c/k^2} \text{ for } k \leq 1.588\times 10^{+8}\ \text{cm}^{-1}$$

(3.96 Å) and C an arbitrary constant;

$$\Phi(k) = (C/12.5)k^{a+b/k+c/k^2}$$

$$\text{for } 1.588\times 10^{+8}\ \text{cm}^{-1} < k < 1.805\times 10^{8}\ \text{cm}^{-1};$$

and $\Phi(k) = 0$ for $k \geq 1.805\times 10^{8}\ \text{cm}^{-1}$ (3.48 Å).

To apply corrections (6) and (7), it is necessary to determine the parameters a, b, and c in Eqs. (3) so that Eq. (2) holds within the experimental uncertainties over the entire range of intensities used in the measurement.

The following expression was used as a criterion for finding a, b, and c in Eqs. (3):

$$S = \frac{1}{n}\sum_{i=1} |I_{\text{calc}}(\phi_i) - I_{\text{exp}}(\phi_i)|/\epsilon_i, \qquad (4)$$

where n is the number of experimental intensities used; $I_{\text{exp}}(\phi_i)$ are selected intensities with corrections (1) through (5) applied; ϵ_i is the experimental uncertainty in $I_{\text{exp}}(\phi_i)$; and the $I_{\text{calc}}(\phi_i)$ are given by Eq. (2) and least-squares fitted in the $I_{\text{exp}}(\phi_i)$. The sum S was minimized as a function of the variables a, b, and c in Eq. (3) for a set of four to six reflected intensities from the reference liquid, using W. C. Davidon's variable-metric-minimization program.[6] Corrections (6) and (7) were applied to the data by using the spectrum function found in this way. Although correction (7) was less than 3% (for Hg) in these measurements, it can be quite dependent on the incident beam spectrum, particularly for strong absorbers (Ref. 5, Fig. 1). Correction (6) is smaller than (7) and also spectrum-dependent but to a lesser extent. Finally, the fully corrected experimental intensities were fitted with two- and three-term exponential functions which were interpolated to find the angles at which the reflected intensity from both mirrors was the same.

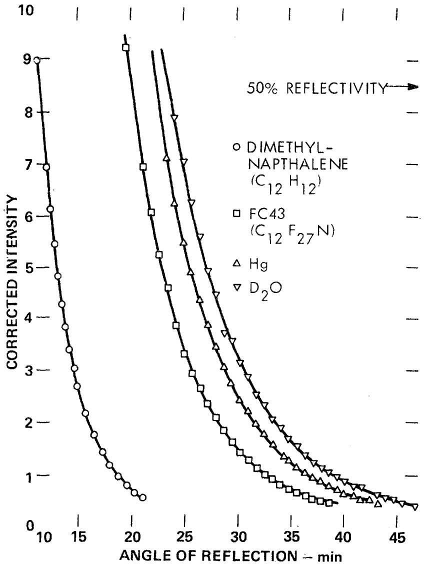

FIG. 1. Reflected intensities.

The mean power of k obtained for the spectrum function $\Phi(k)$ for five different experimental runs was −4.2 at 4 Å, changing to −5.6 at 10 Å. The maximum deviations from these values are about 0.6. The mean power of k at 4 Å is in good agreement with spectra measured at this and other reactors.[3,7] Its increase with increasing neutron wavelength is somewhat larger than previously reported values, but this is expected since the Be filter was at room temperature during these runs. This method of spectrum determination appears to rule out such sources of systematic error as uncertainties in the shape of monochromator or chopper transmission functions due to neutron reflection from the slot walls,[8] but requires some *a priori* knowledge of the spectrum function.

FLUORINE

In this measurement we compared the reflected intensity from fluorocarbon FC43 ($C_{12}F_{27}N$) to that of dimethylnaphthalene ($C_{12}H_{12}$). Figure 1 shows the reflected intensities as a function of incident angle for one of the runs. The solid lines were calculated using Eq. (2) and were least-squares fitted to the data. Using +6.648 ± 0.004 F for the bound-carbon scattering amplitude and −3.719 ± 0.002 F for the bound-hydrogen scattering amplitude,[9] we obtain 5.83 ± 0.17 F for the bound-fluorine coherent neutron-scattering amplitude. It was not feasible to determine the elemental composition of FC43 as accurately as that of our reference hydrocarbon. An attempt was made at purifying the fluid by gas chromatographic techniques, but this was not successful. The error figure reflects mostly the uncertainty in the elemental composition of the fluid, and is considerably higher than those usually attainable by mirror-reflection methods.

MERCURY

In this measurement we compared the reflected intensity from high-purity mercury to that of dimethylnaphthalene. Using the same values of a_C and a_H as for fluorine, we obtain 12.67 ± 0.13 F for the mercury coherent neutron-scattering amplitude. The difference between this value and the one reported[10] in 1963 is due to a simple numerical error and to the use of older values of a_C and a_H. This value is in excellent agreement with a later measurement by Koester[9] who also used mirror techniques. He reported 12.69 ± 0.02 F in 1965.

DEUTERIUM

Our first measurement of deuterium[10] compared the reflected intensity from heavy water to that of dimethylnaphthalene. An error in isotopical analysis gave the purity of the heavy water used as 91.1 ± 0.3-mole % D_2O. The number reported in Ref. 10 (+6.77 ± 0.08 F) was based on this analysis. The error was discovered later and the liquid reanalyzed with the result 96.1 ± 0.3-mole % D_2O. This, with the previously mentioned values of a_C and a_H and a value of 5.80 ± 0.05 F for the oxygen coherent neutron-scattering amplitude,[5] yields

$$a_D = 6.24 \pm 0.11\ \text{F}\ (D_2O \text{ versus } C_{12}H_{12}). \qquad (5)$$

Since mercury was among the liquids used in this run, the ratio ϕ_{D_2O}/ϕ_{Hg} was also determined. If we use an average of Koester's and our results for the coherent neutron scattering amplitude of mercury (that is, $a_{Hg} = 12.68$ F), then

$$a_D = 6.25 \pm 0.10 \text{ F } (D_2O \text{ versus Hg}). \tag{6}$$

The measurement was repeated subsequently, with 99.77-mole %-D_2O material and dimethylnaphthalene as the comparison liquid with the result

$$a_D = 6.18 \pm 0.10 \text{ F } (D_2O \text{ versus } C_{12}H_{12}). \tag{7}$$

Another measurement was also made with high-purity D_2O and mercury as the reference fluid, yielding

$$a_D = 6.20 \pm 0.06 \text{ F } (D_2O \text{ versus Hg}), \tag{8}$$

with a value of 12.68 F for a_{Hg}.
A weighted average of Eqs. (5), (6), (7), and (8) yields our value for the bound-deuterium, neutron coherent scattering amplitude, $a_D = 6.21 \pm 0.04$ F.

SURFACE PURITY

Since the data analysis is based on the bulk properties of the mirror liquid and the neutron penetration is on the order of a few angstroms,[11] it is important to keep the surface as free of impurities as possible. All of the liquid-handling procedures described in Ref. 3, pp. 634–635 were used to insure clean mirror trays and to avoid cross-contamination. The presence of a thin film of vacuum-pump oil on the mirror will lower the $\sum_j N_j a_j$ at the surface and result in smaller coherent scattering amplitudes, since many of these oils have hydrogen-to-carbon ratios near 2 and therefore slightly negative $\sum_j N_j a_j$.

In the event that: (a) the pump-oil vapor pressure in the tray enclosures reached 5 μ (i.e., long pumping times, no cold traps, large vacuum lines, and mirror liquids with vapor pressures lower than 50 μ), and (b) all of this vapor condensed on the enclosure and mirror surfaces, then the oil film on the mirror surface would reach a thickness of 2 Å, which is not enough to form a monomolecular layer. Our liquid-handling procedures should have reduced this film thickness by at least a factor of 10.

An independent check on our surface cleanliness is inherent in the comparisons of mercury, heavy water, and dimethylnaphthalene in the measurement of the deuterium-scattering amplitude. If hydrocarbon solvents and oils had deposited on the mirror surfaces, they would have been absorbed by the dimethylnaphthalene but not by the other two fluids. Equations (5), (6), (7), and (8) show no evidence of systematic error from this source.

CONCLUSION

Combining the coherent scattering amplitude with the total and the incoherent scattering cross sections yields two pairs of values for the quartet (a_+) and doublet (a_-) scattering amplitudes. Recent measurements of the transmission of polarized neutrons through a polarized deuterium target[12] have shown that a_- is less than a_+. Using

$$a_{\text{coh (bound)}} = \tfrac{1}{3}(2a_+ + a_-) = +6.21 \pm 0.04 \text{ F}$$

and

$$\sigma_{\text{incoh (bound)}} = \tfrac{8}{9}\pi(a_+ - a_-)^2 = 2.25 \pm 0.04 \text{ b}^{13},$$

we obtain

$$a_+(\text{free}) = +6.13 \pm 0.04 \text{ F},$$
$$a_-(\text{free}) = +0.15 \pm 0.05 \text{ F},$$

and

$$\sigma_{\text{scatt (free)}} = 3.15 \pm 0.04 \text{ b}.$$

Previous measurements have yielded:

Hurst and Alcock[14]	$a_- = +0.7 \pm 0.3$ F
	$a_+ = +6.38 \pm 0.06$ F
Nikitin *et al.*[15]	$a_- = +0.57 \pm 0.14$ F
	$a_+ = +6.47 \pm 0.14$ F.

These results differ markedly from ours. The Hurst values were determined by measuring the angular variation in the scattered neutron intensity from a deuterium gas target and obtaining the ratio a_-/a_+. Combining this ratio with σ_{total} (epithermal) yields values for a_+ and a_-. A recent evaluation of this experiment by Seagrave[16] suggests that the differences between the Hurst values and ours lies in using too large a value of σ_{total}.

The Nikitin values were obtained by direct determination of the ortho- and para-deuterium scattering cross sections by transmission, allowing the calculation of the a_+ and a_- amplitudes according to Hammermesh and Schwinger.[17] The explanation for the discrepancy between their result and ours may lie in their determination of the ortho-para composition.

A number of theoretical calculations of the doublet and quartet scattering amplitudes have been made. In particular those of Aaron *et al.*,[18] although normalized to the Hurst and Alcock doublet scattering amplitude, are in reasonable agreement with our results.

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[1] M. Hammermesh, Phys. Rev. 77, 140 (1950).

[2] D. J. Hughes, M. T. Burgy, and G. R. Ringo, Phys. Rev. 77, 291 (1950).

[3] W. C. Dickinson, L. Passell, and O. Halpern, Phys. Rev. 126, 632 (1962).

[4] W. C. Dickinson, L. Passell, W. Bartolini, and O. Halpern, Lawrence Radiation Laboratory, University of California Report No. UCRL-6320 (1961).

[5] R. E. Donaldson, L. Passell, W. Bartolini, and D. J. Groves, Phys. Rev. 138, B1116 (1965).

[6] W. C. Davidon, Argonne National Laboratory Report No. ANL-5990 (revised), (1959).

[7] L. B. Borst and L. G. Miller, J. Appl. Phys. 28, 547 (1957).

[8] L. Passell, W. C. Dickinson and W. Bartolini, Rev. Sci. Instr. 32, 870 (1961).

[9] L. Koester, Z. Physik 182, 328 (1965).

[10] W. Bartolini, R. E. Donaldson, and L. Passell, Bull. Am. Phys. Soc. 8, 477 (1963).

[11] D. J. Hughes, Neutron Optics (Interscience Publishing Co., New York, 1954).

[12] V. P. Alfimenkov, V. I. Luschikov, V. G. Nikolenko, Yu. V. Taran and F. L. Shapiro, in the International Conference on Polarized Targets and Ion Sources, Centre d'Etudes Nucleaires de Saclay, 1966 (La Documentation Francaise, Paris, 1967).

[13] W. Gissler, Z. Krist. 118, 149 (1963).

[14] D. G. Hurst and N. Z. Alcock, Can. J. Phys. 29, 36 (1951).

[15] S. J. Nikitin, W. T. Smolyankin, W. Z. Kolganow, A. W. Lebedew, and G. S. Lomkazy, in The First International Conference on Peaceful Uses of Atomic Energy, Geneva, 1955. (The United Nations, New York, 1956), Vol. 2, p. 81.

[16] J. D. Seagrave, Bull. Am. Phys. Soc. 11, 895 (1966).

[17] M. Hammermesh and J. Schwinger, Phys. Rev. 69, 145 (1946).

[18] R. Aaron, R. D. Amado, and Y. Y. Yam, Phys. Rev. Letters 13, 574 (1964).

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Correlated Motions in Simple Classical Liquids

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This paper reports a method for studying correlation functions for simple classical liquids. One atom of the liquid is considered to be an external agent acting on the others, and Liouville's equation is formally solved to obtain their response. From this solution an equation for the velocity autocorrelation function is derived. The method is also applied to the distinct-particle part of the density-density correlation function, $G_d(\vec{x}, t)$. The moment relations for $G_d(\vec{x}, t)$ are in this way made to depend on a hierarchy of equations relating the static correlation functions. When the basic equations derived by this method are approximated further, previously given approximations for $G_d(\vec{x}, t)$ are obtained.

I. INTRODUCTION

In a recent paper[1] Singwi and Sjölander have given an approximate theory of the velocity autocorrelation function of a classical liquid. The philosophy of their method is to consider one atom of the liquid as an external driving agent on the other atoms and to find the response of the others to this one. In I this response was calculated from a simplified kinetic equation for the one particle distribution function of the other atoms.

This paper extends the method of I and has two purposes. First, we show that within the philosophy of I a formal exact solution for the response can be found from the full Liouville equation of the system. To apply this solution to the velocity autocorrelation function, it is necessary to find the change in the density caused by the passage of the particle considered as the external agent. We find, in analogy with linear response theory, but more generally, that this density change is given by a generalized density-density correlation function. This function can be split into self- and distinct-particle parts, just as for the equilibrium function. The approximate solution of I is obtained if we drop the distinct-particle part. Therefore we find that in I any contribution of collective motions to the velocity autocorrelation function was neglected.

The second purpose is to apply this philosophy to the equilibrium density-density correlation function $G(\vec{x}, t)$. This function is of central importance in the theory of radiation scattering by condensed systems.[2] $G(\vec{x}, t)$ can be written as the sum of a self-part $G_s(\vec{x}, t)$ and a distinct-atom part $G_d(\vec{x}, t)$. Since the method of this paper is to treat the response of the other particles to the motion of one, it is naturally suited to calculating the distinct-atom part $G_d(\vec{x}, t)$. We can thus assume that $G_s(\vec{x}, t)$ is known (along with all static correlation functions) and use it in the theory for $G_d(\vec{x}, t)$.

We use the method of the paper to discuss the first four moment relations for $G_d(\vec{x}, t)$, and to show how