Dynamics of Atomic Motions in Liquids and Cold Neutron Scattering*

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The self-correlation function for the motion of an atom in a liquid has been constructed in a manner which simulates the behavior of this function between the two extreme cases, viz., that in a solid and that in a simple diffusive model. Using this function, the differential scattering cross section for cold neutrons has been calculated for liquid lead and compared with available experimental results. It appears that even in a simple liquid like lead the solidlike behavior of atomic motions persists for a considerable time.

THE differential cross section for slow-neutron scattering by a system of interacting particles is given, in Van Hove's[1] formalism, by the Fourier transform of the space-time correlation function $G(\mathbf{r},t)$. This formalism should in principle be adequate to account for neutron scattering by a liquid. However, in the absence of a theory of the liquid state it is not possible to calculate $G(\mathbf{r},t)$. One has thus to take recourse to some simplified model of a liquid and by comparison with experimental results justify it *a posteriori*.

In this communication we are reporting the results obtained on the basis of a model which can simulate the behavior of the self-correlation function between the two extreme cases, viz., that in a solid and that in a simple diffusive model. From the detailed calculations of the scattering of cold neutrons from liquid lead, the only simple liquid for which experimental results are available, it appears that even for a liquid like lead the solidlike behavior of the atomic motions persists for a considerable time.

In an earlier attempt, Singwi and Sjölander[2] assumed a certain time-dependent probability for the persistence of the solidlike motion of the water molecules. Recent experiments of Larsson *et al.*[3] have confirmed the predictions based on such a model.

The coherent scattering cross section is given by

$$\frac{d^2\sigma_{\mathrm{coh}}}{d\Omega d\epsilon}=\frac{a^2_{\mathrm{coh}}}{2\pi\hbar}\frac{k}{k_0}[1+\Gamma(\kappa)]e^{+\hbar\omega/2k_BT}\times\int_{-\infty}^{+\infty}e^{-i\omega t}\exp[-\kappa^2\rho(t)/2], \quad (1)$$

where $\epsilon=\hbar\omega=\hbar^2(\mathbf{k}_0^2-\mathbf{k}^2)/2m$, $\boldsymbol{\kappa}=\mathbf{k}-\mathbf{k}_0$. The coherent correction $[1+\Gamma(\kappa)]$ has been introduced here as in Vineyard's[4] convolution approximation. In obtaining (1) we have used the Gaussian approximation for the self-correlation function, the width being given by

$$\rho(t)=\frac{\hbar^2}{4Mk_BT}+\int_0^t(t-u)\,\mathrm{Re}\langle\mathbf{v}(0)\cdot\mathbf{v}(u)\rangle_T du. \quad (2)$$

The classical velocity correlation function has been used in place of $\mathrm{Re}\langle\mathbf{v}(0)\cdot\mathbf{v}(u)\rangle_T$. Quantum effects of order $\hbar^2$ have thus been neglected. However, the reason for retaining the first term on the right side of Eq. (2) is the fact that $\rho(0)\neq 0$ is of purely quantum mechanical origin. These questions together with the derivation of (2) and the nature of the Gaussian approximation will be examined later on in a detailed paper.

For the classical velocity correlation function we have assumed the following:

$$\langle\mathbf{v}(0)\cdot\mathbf{v}(t)\rangle_T=\frac{d}{dt}\left\{e^{-\gamma t}\frac{9k_BT}{M\omega_D^2}\frac{\mathrm{d}}{dt}\left(\frac{-\sin\omega_Dt}{\omega_Dt}\right)\right\}+\frac{3k_BT}{M}e^{-\beta t}(1-e^{-\alpha t}). \quad (3)$$

The frequency ω_D introduced above corresponds to the Debye frequency in a solid. Of the four parameters, α, β, γ, and ω_D, the first two are related to the diffusion coefficient D through the relation $DM/k_BT=\alpha/\beta(\alpha+\beta)$. The other symbols in (3) have their usual meaning. $\langle\mathbf{v}(0)\cdot\mathbf{v}(t)\rangle_T$ has been so chosen that the width $\rho(t)$ has the right limiting form for both small and large values of t; by varying the parameters it can be made to assume, for intermediate values of time, various forms lying between those for a solid and for a simple diffusing atom obeying Langevin's equation. The characteristic oscillatory behavior of $\rho(t)$ in a solid is here damped through γ. It is fortunate that the choice of at least one of the three parameters does not interfere appreciably with that of the other two; it turns out that the broadening of the quasi-elastic peak is governed mainly by α.

In what follows we shall be concerned only with scattering in liquid lead. Out of the many $\rho(t)$ curves which we have computed using (2) and (3), a few typical ones are shown in Fig. 1. In Fig. 2 are given curves for the differential scattering cross section obtained from Eq. (1), for some typical values of the

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.
[1] L. Van Hove, Phys. Rev. **95**, 249 (1954).
[2] K. S. Singwi and A. Sjölander, Phys. Rev. **119**, 863 (1960).
[3] K. E. Larsson, S. Holmryd, and K. Otnes, International Atomic Energy Agency Symposium on Inelastic Scattering of Neutrons in Solids and Liquids, Vienna, October, 1960 (to be published), Paper *IS*/15.
[4] G. H. Vineyard, Phys. Rev. **110**, 999 (1958).

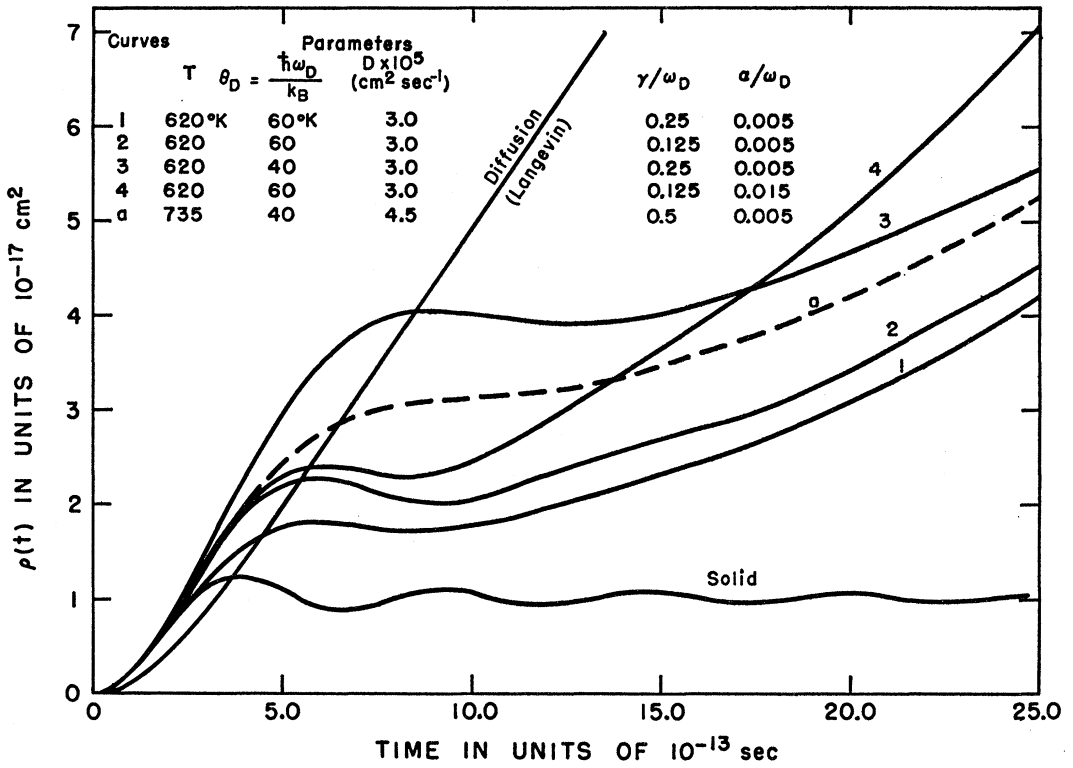

FIG. 1. Width $\rho(t)$ for liquid lead for some values of the parameters, and also for solid lead and for a diffusing atom.

parameters. It should be noted that the broadening of the quasi-elastic peak is mainly determined by α, whereas the magnitude of the inelastic scattering depends both on γ and on ω_D.

In Fig. 3 are shown the parameter values and the curve (solid line) which fits best with the experimental points of Brockhouse.[5] The agreement can be somewhat improved by integrating the calculated curve over the

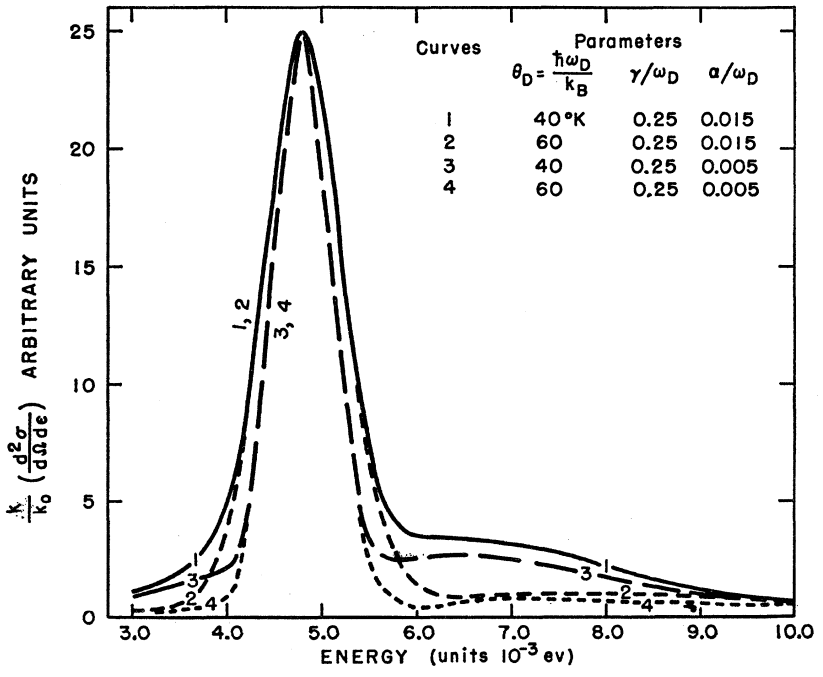

FIG. 2. Differential scattering cross section ($\times k/k_0$) versus outgoing neutron energy for neutrons of incident energy 4.8×10^{-3} ev scattered at 90° by liquid lead at 620°K. Values of the parameters are as shown.

[5] B. N. Brockhouse and N. K. Pope, Phys. Rev. Letters 3, 259 (1959).

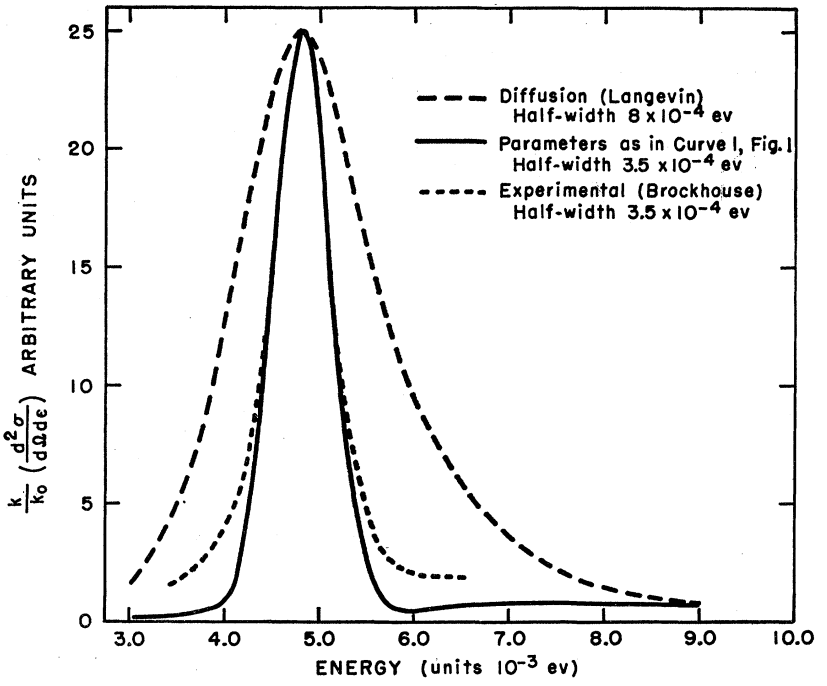

FIG. 3. Differential scattering cross section ($\times k/k_0$) versus outgoing neutron energy for neutrons of incident energy 4.8×10^{-3} ev scattered at 90° by liquid lead at 620°K. Computed and observed curves have been compared.

incident spectrum. In the same figure the dashed curve shows the scattering on the basis of a simple diffusion theory. The set of parameters giving the solid-line curve also gives a good fit with the experimental results of Brockhouse[5] for 1.36-A neutrons scattered at different angles. In fact, the variation in the peak value of the intensity for different angles of scattering, which is due to the coherent correction $[1+\Gamma(\kappa)]$, is reasonably well reproduced in the calculated values. The scattering at angles of 75° and 90° is shown in Fig. 4; these two angles have been chosen to illustrate how the subsidiary peak can be greatly magnified at certain angles of scattering due to the factor $[1+\Gamma(\kappa)]$. It would be desirable to check this experimentally for it provides a clear test for the convolution approximation.

It is evident from the curves of $\rho(t)$ (Fig. 1) which

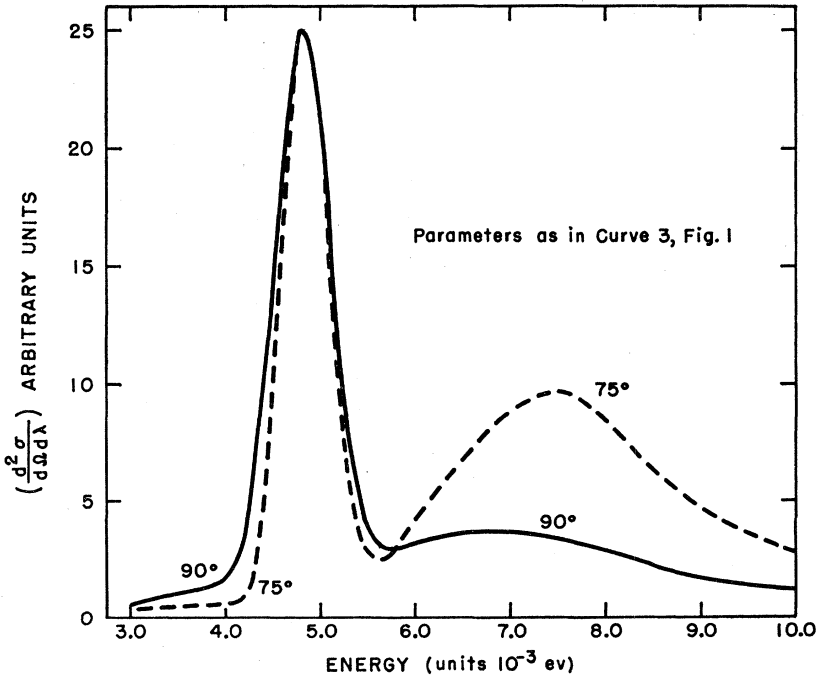

FIG. 4. Differential scattering cross section versus outgoing neutron energy for neutrons of incident energy 4.8×10^{-3} ev scattered at 90° and 75° by liquid lead at 620°K. Note the effect of the coherent factor at 75°.

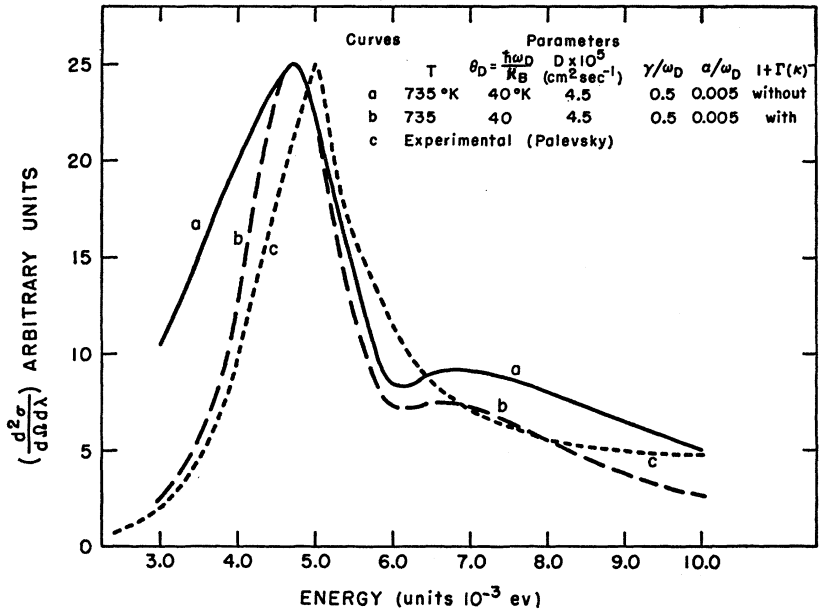

FIG. 5. Differential scattering cross section versus outgoing neutron energy for Be-filtered neutrons scattered at 90° by liquid lead at 735°K. Values of the parameters are as shown.

give the correct scattering cross section that the motion of an atom in a liquid is far from that of a simple diffusive type; it resembles much more the behavior of $\rho(t)$ in a solid except that the oscillatory behavior is very much damped as one would expect on physical grounds. This suggests that an atom in a liquid stays in its equilibrium position, where it performs a complicated oscillatory motion, for a time much longer than its period of vibration. This sedentary behavior is responsible for the small observed broadening of the quasi-elastic scattering, and, presumably, for a structure in the inelastic scattering.

Using the $\rho(t)$ given by the dashed curve of Fig. 1, we have calculated the differential scattering cross section for a beryllium-filtered neutron beam for liquid lead at 735°K and the results are shown in curve *b* of Fig. 5. In the same figure, curve *c* is the experimental curve of Palevsky[6] and it will be seen that the agreement is good. Curve *a* is the calculated curve with the same set of parameters but without the factor $[1+\Gamma(\kappa)]$. An attempt to fit Palevsky's data on the basis of a simple diffusion theory including coherent effects proved unsuccessful.

A more detailed account of this work, including certain theoretical considerations and its implications concerning the liquid state, will form the subject matter of a separate paper. In conclusion we would like to suggest that experiments should be performed with *monochromatic* beams of cold neutrons ($\lambda \gtrsim 4$ A) for simple liquids, to see, besides the quasi-elastic scattering, the structure, if any, of the inelastic scattering. Experiments with filtered beams of neutrons, despite a very sharp cutoff, are less suitable because the broad incident spectrum has the tendency to wipe out the structure and to make the interpretation of even the quasi-elastic scattering somewhat ambiguous. Experiments with liquid vanadium are highly desirable. To bring out the coherent effect, experiments should also be performed for a large range of scattering angles.

[6] H. Palevsky, International Atomic Energy Agency Symposium on Inelastic Scattering of Neutrons in Solids and Liquids, Vienna, October, 1960 (to be published), Paper *IS*/47.