SOVIET PHYSICS JETP VOLUME 24, NUMBER 4 APRIL, 1967

THE ROLE OF DIFFUSION PROCESSES IN THE SCATTERING OF SLOW NEUTRONS IN LIQUIDS

G. K. IVANOV

Institute for Chemical Physics, Academy of Sciences, U.S.S.R.

Submitted to JETP editor March 17, 1966

J. Exptl. Theoret. Phys. (U.S.S.R.) 51, 1120-1126 (October, 1966)

The differential cross section for incoherent scattering of slow neutrons in liquids is calculated by splitting up the whole region of motion of a scattering atom into repeating, statistically independent, regions. Both monatomic and molecular liquids are treated. For the monatomic liquids, atomic vibrations, diffusion of the centers of vibration, and arbitrary shifts of the particle from one equilibrium position to another are taken into account. In molecular liquids, in addition to the types of motion just enumerated, we also consider reorientation of the molecule about various axes. The results explain the fine structure of the observed spectra from quasielastic scattering of neutrons in water.

A great many investigations have been made of quasielastic scattering of slow neutrons in liquids. These have made it possible to determine some very important characteristics of liquids.

In the theoretical analysis of processes of scattering of neutrons in liquids extensive use is made of the concept of a classical space-time correlation function G(**r**, t). According to Van Hove[1] these functions are uniquely related (by a Fourier transformation) to the differential scattering cross section, in which one assigns the energy ϵ and momentum $\boldsymbol{\kappa}$ transferred (or taken up) by the neutron. Using the functions G(**r**, t) obtained from some equations of motion, explanations were given for the scattering of neutrons by continuous diffusion (in the paper of Vineyard[2]), discontinuous diffusion (in the work of Chudley and Elliott[3]), Langevin diffusion (in the work of Rahman, Singwi and Sjölander[4]). Studies were also made of the scattering of neutrons by particles whose behavior is described by the Boltzmann kinetic equation (cf. the work of Nelkin and Ghatak,[5] Gibbs and Ferziger[6]).

It should, however, be stated that none of these equations contains completely all the elements of the motion of particles of a liquid. One therefore frequently resorts to a phenomenological description of G(**r**, t).[7] In getting G(**r**, t) one also can combine different correlation functions. Thus, Singwi and Sjölander,[8] using two correlation functions, describing continuous diffusion and vibration, respectively, took account of quasivibrational states of the atoms in addition to their continuous diffusion. This result is widely used for analysis of experiments, but, as will be shown below, also contains some arbitrary assumptions.

In avoiding arbitrary simplifications in the initial assumptions of the theory, in the present paper we propose a different approach to the problem of scattering of neutrons in liquids: the differential cross section is calculated directly (omitting the determination of G(**r**, t)) by breaking up the region of motion of the atoms into repeating statistically independent parts. The advantage of this method is that it is possible to include any elements of the motion of the atoms, which is very important in treating molecular liquids, for which the previous results[2-8] are essentially invalid.

1. DERIVATION OF GENERAL FORMULAS

We shall consider incoherently scattering liquids, which include all water-containing liquids and some of the liquid metals. In this case it is sufficient to consider only the behavior of a single atom in the medium, where the general expression for the differential cross section per unit range of angle o and energy ϵ can be written as follows:

$$\frac{d^2\sigma}{d\varepsilon do} = a^2 \frac{k}{2\pi k_0} \int\limits_{-\infty}^{\infty} e^{-i\varepsilon t} \left(e^{i\boldsymbol{\varkappa}\mathbf{r}(t)} e^{-i\boldsymbol{\varkappa}\mathbf{r}(0)} \right) dt. \qquad (1)$$

Here a is the amplitude for incoherent neutron-nucleus scattering, $\mathbf{k}_0$ and $\mathbf{k} = \mathbf{k}_0 - \boldsymbol{\kappa}$ are the neutron momenta in the initial and final states (we set Planck's constant equal to one throughout), **r**(t) is the operator for the particle position at time t. The parentheses in (1) denote an average over the state of the scattering atom in the medium.

The whole region of motion of the atom in the liquid can be described in general terms as consisting of a series of repeating statistically independent sections. For example, we can assert that in molecular liquids the translational displacements of the molecules are repeated, each displacement being statistically independent of the preceding one. In the interval between translations, vibration and reorientation of the molecule occur. We therefore assume that each of the segments can have a complex structure, i.e., may include a large number of different elements of the motion.

Using these properties of the motion of atoms in liquids, we can transform (1) to the following form:

$$\frac{d^2\sigma}{d\varepsilon\, do} = a^2 \frac{k}{2\pi k_0}\left[\frac{1}{1-q} Q + \text{c.c.}\right], \tag{2}$$

where

$$q = \langle e^{-i\varepsilon t}\left(e^{i\varkappa \mathbf{r}(t)} e^{-i\varkappa \mathbf{r}(0)}\right)\rangle, \quad Q = \left\langle \int_0^t e^{-i\varepsilon t}\left(e^{i\varkappa \mathbf{r}(t)} e^{-i\varkappa \mathbf{r}(0)}\right) dt \right\rangle \tag{3}$$

are averages of the respective quantities over all possible characteristics of the repeated sections of the motion; t is the time spent by the particle in a given section.

The angular brackets in (3) denote a quantum mechanical average of the operators $e^{i\kappa\cdot\mathbf{r}(t)} e^{-i\kappa\cdot\mathbf{r}(0)}$. The latter can be replaced by classically commuting quantities if we neglect the recoil experienced by the atom in colliding with the neutron. The classical approximation and the associated notion of a trajectory can be used with full justification in considering stochastic translational and rotational displacements of molecules in so-called "quasicrystalline" liquids, which will be the main subject of the present paper. In "quasicrystalline" liquids the average time spent by the atom in vibrational states, τ_0, is much greater than the path time τ_1: $\tau_0 \gg \tau_1$. Thus the quantitative criterion arising from (3) for neglecting recoil during the flight is

$$\varepsilon\tau_0 \gg \varkappa^2\tau_1 / 2M \tag{4}$$

(M is the mass of the moving particle), which is well satisfied in the region of scattering in which we are interested ($\epsilon \sim 10^{-3}$ eV, while $\kappa^2/2M \sim 10^{-3}$ (m/M) eV, where m is the neutron mass).

2. MONATOMIC LIQUIDS

According to Frenkel,[9] the trajectory of a particle in a monatomic liquid is a kinked line, as in the case of gas. The difference from the case of a gas is that at each kink the particle pauses, and during the pause carries out rapid oscillations about some slowly moving center of equilibrium. The motion of the center of the vibration is caused by the recoil suffered by the atom and its surroundings because of other randomly moving atoms.

Thus, the sections of the trajectory selected by us in this case include two elements: a quasivibrational state characterized by the vibration amplitude u(t) and motion l′(t) of the center of the vibration, and an arbitrary displacement of the atom l(t). Let τ_0 be the average lifetime of the atom in the vibrational state and τ_1 the time spent by the atom in the state of displacement. Then applying formula (2) we can write[1)]

$$\frac{d^2\sigma}{d\varepsilon\, do} = a^2 \frac{k}{2\pi k_0}\left\{\frac{1}{1-\alpha\beta}\left[\frac{\tau_0}{\tau_0+\tau_1}(B+\beta A) + \frac{\tau_1}{\tau_0+\tau_1}(A+\alpha B)\right] + \text{c.c.}\right\}. \tag{5}$$

Here

$$\alpha = \langle e^{-i\varepsilon t} e^{i\varkappa \mathbf{l}(t)}\rangle_{\text{tr}} \qquad A = \left\langle \int_0^t e^{-i\varepsilon t} e^{i\varkappa \mathbf{l}(t)}\, dt \right\rangle_{\text{tr}} \tag{6}$$

determine the contribution of the discontinuous displacements of the particles, and the coefficients

$$\beta = \quad e^{-i\varepsilon t}\left(e^{i\varkappa \mathbf{u}(t)} e^{-i\varkappa \mathbf{u}(0)}\right) e^{i\varkappa \mathbf{l}'(t)}\rangle_{\text{vib}},$$

$$B = \left\langle \int_0^t e^{-i\varepsilon t}\left(e^{i\varkappa \mathbf{u}(t)} e^{-i\varkappa \mathbf{u}(0)}\right) e^{i\varkappa \mathbf{l}'(t)}\, dt \right\rangle_{\text{vib}} \tag{7}$$

take account of the quasivibrational states. The factors $\tau_0/(\tau_0 + \tau_1)$ and $\tau_1/(\tau_0 + \tau_1)$ characterize the probabilities for finding the particle at time t = 0 in the quasivibrational state or in flight.

The quasivibrational motion can be described quite accurately, since the motion of the center of vibration caused by stochastic wandering of a large group of atoms is well described by the continuous diffusion model, i.e., by a single parameter, the diffusion coefficient D_1, while the vibrations around the position of equilibrium are taken into account through the Debye-Waller factor e^{-2W}.[2)] Thus, assuming that the distribution of lifetimes in the vibrational state has the form $\tau_0^{-1}\exp(-t/\tau_0)$, after integrating (7) we can write

---

[1)] Formula (5) coincides formally with formula (11) of Singwi and Sjölander, [8] where it was gotten by using correlation functions and analyzed for a special choice of these functions.

[2)] The quantity $2W = \kappa^2\bar{R}^2/6$, where $\bar{R}^2$ is the mean square displacement because of vibrational motion.

$$\beta = \frac{B}{\tau_0} = e^{-2W} \frac{1}{1 + \varkappa^2 D_1 \tau_0 + i\varepsilon\tau_0}. \tag{8}$$

In general we have considerably less information about the path functions α and A in (6). But it is easy to show that when $\kappa l_0 < 1$ (where l_0 is the characteristic elementary path of the atom) the details of the behavior of the atom in the interval l_0 are unimportant and the cross section is given by the simple formula of diffusion theory in accordance with[2,8]:

$$\frac{d^2\sigma}{d\varepsilon\, do} = a^2 \frac{k}{k_0} \frac{1}{\pi} \frac{\varkappa^2 D}{(\varkappa^2 D)^2 + \varepsilon^2}, \tag{9}$$

where D is the diffusion coefficient, i.e., the mean square displacement of the particle per unit time:

$$D = \left(\frac{\overline{l^2} + \overline{R^2}}{6} + D_1 \tau_0 \right) \Big/ (\tau_0 + \tau_1). \tag{10}$$

The quasielastic broadening of the peaks of incident neutrons are described by the diffusion coefficient only in the region of very small momentum transfers; consequently, from measurements at a single scattering angle one can reliably determine the diffusion coefficient only in this region of κ, i.e., practically only when $\kappa < 0.5$ Å^{-1}. When $\kappa l_0 > 1$, formula (9) does not hold. We shall consider this region of momentum transfers in the most important case of "quasicrystalline" liquids, when $\tau_0 \gg \tau_1$. From (5) we have, when $\tau_0 \gg \tau_1$,

$$\frac{d^2\sigma}{d\varepsilon\, do} = a^2 \frac{k}{k_0} \frac{1}{\pi} \frac{e^{-2W}\Gamma(\varkappa)}{[\Gamma(\varkappa)]^2 + \varepsilon^2}, \tag{11}$$

i.e., the energy dependence is a Lorentzian with a halfwidth (at half maximum) of

$$\Gamma(\varkappa) = \frac{1}{\tau_0} [1 + \varkappa^2 D_1 \tau_0 - \alpha(\varkappa) e^{-2W}], \tag{12}$$

where

$$\alpha(\varkappa) = \langle e^{i\varkappa \mathbf{l}} \rangle_{\text{tr}} = \int e^{i\varkappa \mathbf{l}} F(\mathbf{l})\, d\mathbf{l}, \tag{13}$$

F(l) is the normalized distribution function for lengths of free paths of atoms. Together with the diffusion coefficient, this function is the most important microdynamical characteristic of the liquid.

In the paper of Singwi and Sjölander[8] (this paper does not include diffusion of the centers of vibration, i.e., $D_1 = 0$) and the work of Oskotskiĭ [10] ($D_1 \neq 0$) a formula is derived, similar to (2), with

$$\alpha(\varkappa) = 1 / (1 + \varkappa^2 D' \tau_1), \quad D' = \overline{l^2} / 6\tau_1. \tag{14}$$

This form of the function α can be obtained from (6) if one assumes that the motion of the atom in the interval between two quasivibrational states is described by a continuous diffusion model, i.e., is characterized by a large number of small, statistically independent displacements, and if we assume that the distribution over lifetimes in the diffusing state has the form $\tau_1^{-1} \exp(-t/\tau_1)$. Thus, the model of Singwi and Sjölander,[8] in the form in which everyone uses it for analysis of experimental data, essentially does not take account of the discontinuous diffusion mechanism. In analyzing neutron scattering in liquids there is no basis for using formula (14) or any other specific dependence $\alpha(\kappa)$ in (12), since $\alpha(\kappa)$ and F(l) are unknown functions to be determined from the neutron experiment.

3. MOLECULAR LIQUIDS

Most of the existing work on incoherent scattering of neutrons is for molecular liquids, such as water,[11,12] glycerine,[13] methyl and ethyl alcohol.[14] In analyzing these experiments one must take account of the stochastic reorientation of the molecules.

Let us assume that in the interval between two successive abrupt translational displacements of the molecule, there is a sizable probability for reorientation of the molecule around some axis (as is usually the case in molecular crystals). We also assume that all the displacements are instantaneous, the atoms of the molecule spend their time essentially in quasivibrational states (we are considering a "quasicrystalline" liquid). Then, assuming that each translation represents the start of a new independent cycle of motion, using formula (2) we can write

$$\frac{d^2\sigma}{d\varepsilon\, do} = a^2 \frac{k}{k_0} \frac{1}{2\pi} \left\{ \frac{1}{1 - \alpha p} P + \text{c.c.} \right\}, \tag{15}$$

where $\alpha = \langle e^{i\boldsymbol{\kappa} \cdot \mathbf{l}} \rangle_{\text{tr}}$ characterizes the translational component of the motion of the molecule, while p and P describe the total contribution to the cross section of all possible reorientations of the molecule around the z axis. According to the general formulas (2) and (3) we have for p and P:

$$p = \langle \exp [-i\varepsilon t + i\varkappa\rho \sin\theta \\ \times (\sin\varphi - \sin\varphi_0)] W(\varphi, \varphi_0, t) e^{i\varkappa \mathbf{l}'(t)} \rangle,$$

$$P = \left\langle \int_0^t \exp [-i\varepsilon t + i\varkappa\rho \sin\theta \right. \\ \left. \times (\sin\varphi - \sin\varphi_0)] W(\varphi, \varphi_0, t) e^{i\varkappa \mathbf{l}'(t)} dt \right\rangle. \tag{16}$$

Here $\kappa \sin\theta$ is the component of the vector $\boldsymbol{\kappa}$ in the plane of rotation, ρ is the distance from the scattering atom to the rotation axis, φ and φ_0 are angles characterizing the position of the atom in the plane of rotation: $W(\varphi, \varphi_0, t)$ is the probability that a molecule, initially oriented at an angle φ_0 in the plane of rotation at $t = 0$, is at angle φ at time t. In the case of uniaxial rotation, $W(\varphi, \varphi_0, t)$ has the following form[15] (in the formula given below, in addition to the result of[15] we also include vibration of the atoms around the positions of equilibrium):

$$W(\varphi, \varphi_0, t) = e^{-2W} \sum_{m=-\infty}^{\infty} \exp\left\{-\frac{t}{T_1}(1 - A_m) - im(\varphi - \varphi_0)\right\}. \tag{17}$$

Here T_1 is the mean life of the molecule for rotation about a given axis;

$$A_m = e^{-2W} \int_{-\pi}^{\pi} f(\varphi)\, e^{im\varphi}\, d\varphi, \tag{18}$$

where $f(\varphi)$ is the distribution of the angles of rotation. If the molecule carries out a unit rotation at a fixed angle χ, $A_m = e^{-2W} \cos m\chi$. Substituting (17) in (15) and considering that the probability distribution of lifetimes of the molecules for translational displacements has the form $T^{-1} \exp(-t/T)$, while the motion of the center of vibration is described by a continuous diffusion model with diffusion coefficient D_1, after some transformations we get

$$\frac{d^2\sigma}{d\varepsilon\, do} = a^2 \frac{k}{2\pi k_0}\left\{ e^{-2W}\left(1 - \frac{\alpha(\varkappa) e^{-2W}}{T}\left[\sum_m \frac{f_m(\varkappa\rho)}{\Gamma_m(\varkappa) + i\varepsilon}\right]\right)^{-1} \times\left[\sum_m \frac{f_m(\varkappa\rho)}{\Gamma_m(\varkappa) + i\varepsilon}\right] + \text{c.c.}\right\},$$

$$\Gamma_m(\varkappa) = \frac{1}{\tau}(1 - \gamma A_m) + \varkappa^2 D_1,$$

$$\tau = \frac{TT_1}{T + T_1}, \qquad \gamma = \frac{T}{T + T_1},$$

$$f_m(\varkappa\rho) = \int_0^1 J_m{}^2(\varkappa\rho\sqrt{1 - x^2})\, dx. \tag{19}$$

A graph of the function $f_m(\kappa\rho)$ for $m = 0, 1, 2$ is shown in Fig. 1 of[16].

If the quantity $\gamma = T/(T + T_1)$ characterizing the probability of reorientation of the molecule after a quasivibrational state is small ($\gamma \ll 1$), $\tau = T$, $\Gamma_m = 1/T + \kappa^2 D_1$ and, since $\Sigma_m f_m(\kappa\rho) = 1$, formula (19) goes over into the earlier result (11) describing vibrations and stochastic translational displacements of the particles. In this case molecular liquids are similar to monatomic liquids with respect to scattering of neutrons.

When $\gamma \sim 1$, the rotational displacements of the molecules have an important effect on the spectra of scattered neutrons. In particular, they lead to a change in the diffusion coefficient describing the process for small κ. In this case we again have a Lorentz curve with half-width $\Gamma(\kappa) = \kappa^2 D$, where $D = (\overline{l}^2 + \overline{l}^2_{\text{rot}} + \overline{R}^2)/6T + D_1$, where $\overline{l}^2_{\text{rot}} = 2\gamma\rho^2(1 - A_1)/(1 - \gamma A_1)$, i.e., $\overline{l}^2_{\text{rot}} = 4\gamma\rho^2 \sin^2(\chi/2)$ if $\gamma \ll 1$, and $\overline{l}^2_{\text{rot}} = 2\rho^2$ if γ is close to unity. These values for $\overline{l}^2_{\text{rot}}$ are easily gotten from geometrical arguments.

The role of rotational diffusion in molecular liquids may be very great. In studying scattering of neutrons in glycerine[13] it was found, for example, that the observed diffusion coefficients were approximately 100 times greater than those determined from data on the liquid. This is a direct indication that the displacements of the atoms in glycerine are almost entirely due to reorientation of the molecules, i.e., in this case $\overline{l}^2_{\text{rot}} \gg \overline{l}^2$ in the formula for D.

In the region of $\kappa > 2\text{Å}^{-1}$ (most measurements of quasielastic peaks refer essentially to this region) the quantity $\alpha(\kappa)$ may be assumed to be small compared to one, so that

$$\frac{d^2\sigma}{d\varepsilon\, do} = a^2 \frac{k}{k_0} \frac{e^{-2W}}{\pi} \left\{ \sum_m \frac{f_m(\varkappa\rho)\, \Gamma_m(\varkappa)}{[\Gamma_m(\varkappa)]^2 + \varepsilon^2} \right\}, \tag{20}$$

i.e., the cross section is a simple superposition of several Lorentz curves with different intensities and widths.

There are many indications at present that the scattered spectrum is not described accurately by a Lorentz curve, and finally there are the very accurate measurements of Golikov et al,[12] which show directly that the spectrum of the scattered neutrons from water for $\kappa \approx 2\text{Å}^{-1}$ consists of two lines with halfwidths 0.3×10^{-3} eV and 0.6×10^{-3} eV (this result is described in detail in the monograph of Turchin.[17])

This fact finds a straightforward explanation on the basis of formula (20). In fact, if we assume that in water one can have reorientation of the H_2O molecule around one of the hydrogen bonds OH...O, one should observe in the scattered spectrum, when $\kappa = 2\text{Å}^{-1}$ (i.e., when $\kappa\rho \approx 2$), two Lorentzian lines (cf. Fig. 1 of[16]) with maxima of almost equal intensity and a third line with very low intensity (it also appears to have been observed in the spectrum[12]).

The author is grateful to Yu. S. Sayasov for discussion of the results.

[1] L. Van Hove, Phys. Rev. 95, 249 (1954).
[2] G. H. Vineyard, Phys. Rev. 110, 999 (1958).
[3] C. T. Chudley and K. I. Elliott, Proc. Phys. Soc. (London) 77, 353 (1961).

[4] A. Rahman, K. S. Singwi and A. Sjölander, Phys. Rev. **126**, 986, 997 (1962).

[5] M. Nelkin and A. Ghatak, Phys. Rev. **137**, 135A (1964).

[6] A. G. Gibbs and I. Ferziger, Phys. Rev. **138**, 701A (1965).

[7] P. A. Egelstaff and P. Schofield, Nucl. Sci. and Eng., **12**, 260 (1962).

[8] K. S. Singwi and A. Sjölander, Phys. Rev. **119**, 863 (1960).

[9] Ya. I. Frenkel', Selected papers, Izd. Acad. Sci. USSR, **3**, 1959.

[10] V. S. Oskotskiĭ, FTT **5**, 1082 (1963), Soviet Phys. Solid State **5**, 789 (1963).

[11] M. Sakamoto, B. M. Brockhouse, R. H. Johnson and N. K. Pope, J. Phys. Soc. Japan **17**, Suppl. B, part II, p. 370 (1962).

[12] V. V. Golikov, F. L. Shapiro, A. Shkatula and Yu. Yanik. Reports of working session on physics of slow neutrons, JINR, Dubna, 1962, p. 184.

[13] K. E. Larsson and V. Dahlborg, Inelastic Scattering of Neutrons, Chalk River 1962 Symposium, IAEA, Vienna, 1963, p. 317.

[14] D. H. Saunderson and V. S. Rainey, Inelastic Scattering of Neutrons, Chalk River 1962 Symposium, IAEA, Vienna, 1963, p. 413.

[15] E. N. Ivanov and K. A. Valiev, Optika i Spektroskopiya **19**, 897 (1965).

[16] G. K. Ivanov, JETP **50**, 726 (1966), Soviet Phys. JETP **23**, 481 (1966).

[17] V. F. Turchin, Mediennye neitrony (Slow Neutrons), Atomizdat 1963, p. 255; transl. Daniel Davey, N. Y., 1965.

Translated by M. Hamermesh
135