

# INELASTIC SCATTERING OF NEUTRONS IN SIMPLE LIQUIDS

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Aspects of the scattering of neutrons in simple liquids are discussed. Elastic, quasielastic, and inelastic scattering are analyzed in such liquids in an effort to single out the most profitable directions for future studies. The necessary optical parameters of the experimental apparatus are estimated, and those regions of  $(\hbar\omega - Q)$  space which seem particularly interesting are pointed out.

## INTRODUCTION

The simplest liquids, e.g., the liquid metals and the noble gases in the liquid state, have been chosen for study by means of neutron scattering because in these liquids there are no molecules and thus no intramolecular motion to complicate observation of the microscopic dynamics characteristic of the liquids. By analyzing the spectrum of neutrons scattered inelastically in a simple liquid, we can obtain information about collective motion and the diffusion mechanism. There have been several recent reviews of experimental results (e.g., [1, 2]), but some questions which follow from the analysis of the results available deserve further attention. For example, it seems desirable to discuss whether more information of this type can be obtained and, in particular, whether it is ambiguous; we take up these problems below.

## 1. ELASTIC SCATTERING

In a study of the physical properties of a simple liquid, particularly of a liquid metal, it is very important to determine the structure. The structure is studied by means of x-ray diffraction and neutron diffraction, in a relatively simple experimental procedure: A monochromatic radiation beam is directed onto the sample, and the angular dependence of the intensity of the radiation scattered elastically and coherently is measured. As a rule, such measurements require a two-axis spectrometer.

In a neutron scattering experiment the intensity which is measured is proportional to the effective differential cross section, which in turn is governed by elastic and inelastic, coherent and incoherent scattering events which depend on the vector  $Q$  ( $Q = k_0 - k$ , where  $k_0$  and  $k$  are the wave vectors of the incident and scattered neutrons). The inelastic scattering is frequently slight, and the incoherent scattering is frequently isotropic, so by measuring the intensity of this type of scattering at an angle  $Q = 0$  and by subtracting this intensity from the scattering intensity at a given angle, one can single out the coherent scattering component. This procedure is relatively simple, although it is not always possible in practice to carry it out sufficiently accurately. An example of this type of study of the structure of simple liquids is a recently published study [3] on neutron diffraction by liquid copper. It was found that heating the sample from near the melting point (1086°C) to 1492°C does not qualitatively change the diffraction pattern: the positions of the maxima do not change. The position of the first maximum corresponds to a value of  $Q = 3 \text{ \AA}^{-1}$  and lies at the position corresponding to the first (111) maximum of the diffraction pattern of crystalline copper. Heating simply changes the intensities of these maxima. These results agree qualitatively with those obtained in a study of other liquid metals [4, 5]. As the temperature of lead is raised from 340

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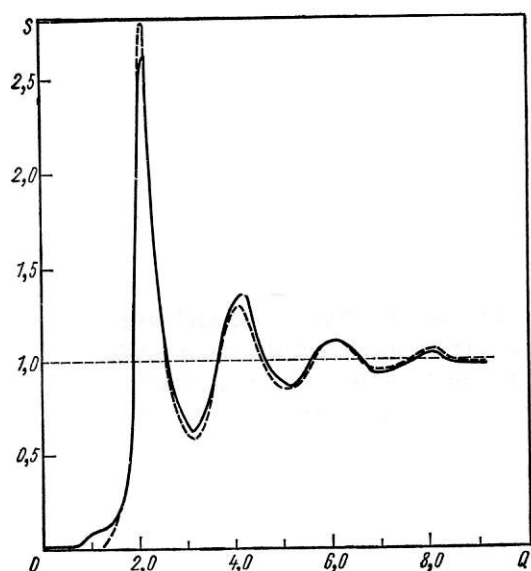


Fig. 1. Structure factor for lead according to neutron scattering (solid curve) and x-ray scattering (broken curve) [4].

to 1100°C, the first and second maxima retain their positions, and only the third shifts, but the shift is slight, close to the experimental error.

This qualitative agreement is particularly important for the case of lead, for the experiment has been analyzed particularly carefully for this case. In addition to experimental effects such as multiple scattering, neutron absorption in the target, etc., North et al. [5] took into account the fact that in a two-axis experiment, the detector detects both elastically and inelastically scattered neutrons. They used the results of [6] to extract the actual value of the structure factor from the experimental data. They assumed that the energy transferred during elastic scattering was much less than the energy of the incident neutrons and that the detector efficiency obeyed a  $1/v$  law. The accuracy with which the structure factor can be determined by this method was evaluated in [5]. Taking into account all the experimental factors, North et al. concluded that the deviation from the actual value in lead did not exceed 3%. However, it was found in a study of liquid gallium [7] that the inelastic contribution is more important than predicted by that approximation of the theory of [6] which they used. Accordingly, the indicated error was evidently too low.

Account of the data in [3, 5] shows an account of inelastic scattering in the case of lead is not a sufficient basis for extracting the expected distortion of the diffraction pattern due to the heating. This circumstance requires a review of the accuracy with which the structure factor is determined in a neutron-scattering experiment.

By comparing the differential cross sections for coherent elastic scattering of neutrons and x rays, one can determine the x-ray form factor  $S(Q)$  [4]. Figure 1 compares the experimental  $S(Q)$  values obtained from neutron and x-ray scattering [5]. If the estimated error is correct, there is a clear discrepancy in the range  $2 \text{ \AA}^{-1} < Q < 4 \text{ \AA}^{-1}$  between the two groups of experimental results. If this discrepancy is not due to experimental errors, it shows that the form factor depends on the method used to determine it. A refinement of the experimental procedure, including the procedure used to analyze the data as well as the procedure used to acquire them, will aid the understanding of this point and will improve our understanding of the physical properties of this scatterer.

One of the most promising approaches for improving the experimental data on coherent elastic scattering seems to be the use of elastic diffraction, discussed several years ago by Caglioti [8]. This method is successful because very high-resolution spectrometric apparatus can be used; more precisely, apparatus having the resolution optimum for the given region of  $(h\omega - Q)$  space and for the given scatterer can be used. The results obtained in a study [7] of liquid gallium by a conventional method and by elastic diffraction are shown in Fig. 2; this figure shows the advantage of the elastic-diffraction method only qualitatively, for the results are partially masked by the resolution value (on the order of 5%) and by the method used to correct for the resolution.

We note that the method proposed in [9] and subsequently refined can be used to determine the resolution experimentally and to find the approximately optimum experimental conditions. On the basis of these results we can hope that the fundamental advantages of the elastic diffraction method for studying liquid structure will find extensive use in the future.

## 2. QUASIELASTIC SCATTERING

In several simple liquids the use of quasielastic neutron scattering can reveal the diffusion mechanism. With this goal in mind, the investigator determines the  $Q^2$  dependence of the half-width of the quasi-

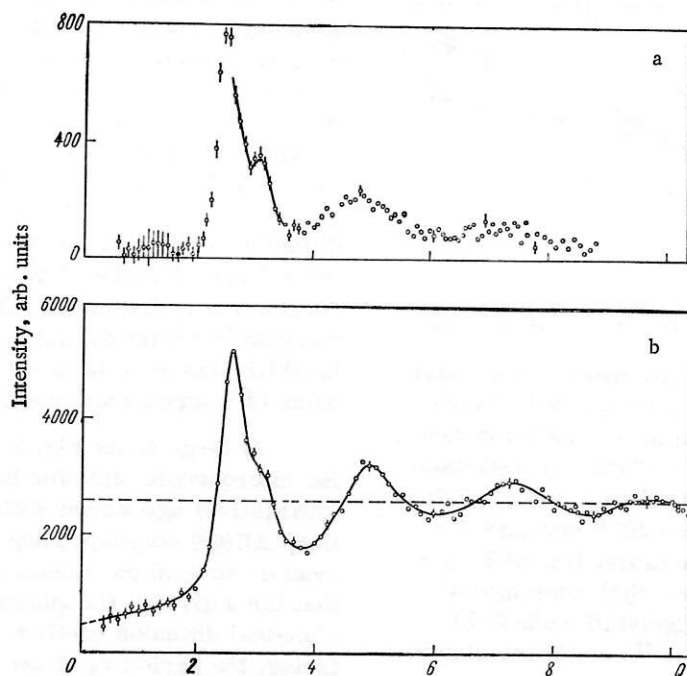


Fig. 2. Neutron scattering in liquid gallium measured by the elastic-diffraction method (a) and by the conventional method (b) [8].

elastic peak. Analyzing the published data on this question, we can conclude that the information which has been achieved in the studies of  $\Delta E(Q^2)$  is ambiguous. The explanation is apparently to be found in the inadequacy of the theoretical approaches to the treatment of diffusion and in the formulation of the experiments. To justify this assertion, we restrict the discussion to the results obtained in a study of quasi-elastic incoherent scattering. From a quite convincing analysis of only a single liquid we can reach certain conclusions regarding the requirements imposed on future experiments.

Among liquid metals sodium has been studied particularly thoroughly. The first results regarding the atomic motion in this liquid were reported by Cocking [10], whose experiments were carried out (with an incident-neutron energy of 4.1 MeV and scattering angles from  $0^\circ$  to  $90^\circ$ ) to cover the small- $Q$  range ( $0 < Q < 2 \text{ \AA}^{-1}$ ). The spectral width of the incident beam was assumed to be about  $3 \cdot 10^{-4} \text{ eV}$ . In the range  $0 < Q < 1.5 \text{ \AA}^{-1}$  the structure factor for sodium increases from 0 to roughly 0.2. The effective coherent-scattering cross section is 1.85 b. These two circumstances led Cocking to conclude that the quasielastic peak observed at small scattering angles was due primarily to incoherent scattering. Coherent scattering is important only at large scattering angles, i.e., near the upper limit of the  $Q$  range studied. In the region of purely incoherent scattering the experimental data were compared with calculated values predicted by the Egelstaff-Schofield model [11]. It was found that the interaction time  $c$  — the characteristic parameter for this model — increases with increasing temperature. It was concluded on the basis of the temperature dependence of  $c$  that free diffusion was the characteristic process for liquid sodium.

Additional data on the quasielastic scattering of neutrons in liquid sodium were reported in [12, 13]. Figure 3 shows Cocking's results (obtained at a sample temperature of 388°K [12]), along with theoretical curves calculated on the basis of four models for the diffusion mechanism: the continuous-diffusion model [14], the jump-diffusion model [15], the jump-diffusion model with an account of the motion of the dynamic equilibrium center [16], and the Egelstaff-Schofield model [11]. In the experimental results of [12] the spectral width  $\Delta E_0$  of the incident beam is in the range  $6 \cdot 10^{-5}$ – $2 \cdot 10^{-4} \text{ eV}$ , while that in [13] is in the range  $(1.25\text{--}2.4) \cdot 10^{-3} \text{ eV}$ . Since both studies deal with the small- $Q$  range, the uncertainty  $\Delta Q$  in the values is very important in a comparison of the experimental and theoretical data. In [13] this  $\Delta Q$  value is  $0.06 \text{ \AA}^{-1}$ .

From Fig. 3 we see that for very small  $Q$  (less than  $0.5 \text{ \AA}^{-1}$ ) these data qualitatively obey Fick's law, according to which diffusion can be described by a single parameter — the diffusion coefficient. The devia-

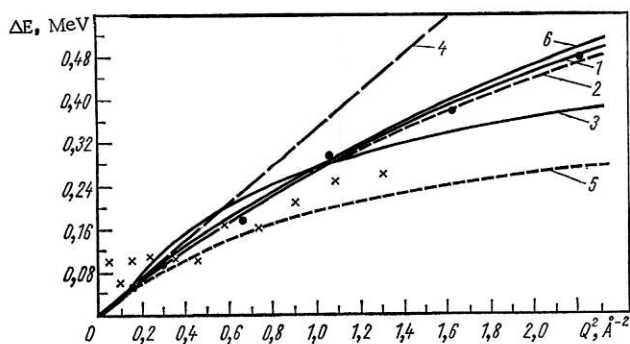


Fig. 3. Dependence of the half-width of the quasielastic peak in liquid sodium on  $Q^2$ . Filled circles) Measurements of [12] at  $T = 388^\circ\text{K}$ ; crosses) measurements of [13] at  $T = 375^\circ\text{K}$ . 1) Oskotskii model [16] with  $\tau_0 = 1.8 \cdot 10^{-12}$  sec and  $f = 0.7$ ; 2) Oskotskii model with  $\tau_0 = 4 \cdot 10^{-12}$  sec and  $f = 0.6$ ; 3) the Singwi-Sjolander model [15] with  $\tau_0 = 1.5 \cdot 10^{-12}$  sec; 4) the Singwi-Sjolander model with  $\tau_0 = 2 \cdot 10^{-12}$  sec; 5) Egelstaff-Schofield model [11] with  $c = 1.47 \cdot 10^{-12}$  sec; 6) the simple-diffusion model.

Debye-Waller factor is governed by the integral intensity of the quasielastic peak. Under the assumption  $\tau_1 \ll \tau_0$  and for a given  $D$ , the quantity  $\Delta E$  depends on only the single parameter  $\tau_0$ , whose value is found for the condition for best agreement between the theoretical and experimental data. Analyzing experimental data for the range  $Q^2 < 1.4 \text{ \AA}^{-2}$ , Randolph [13] found a value of  $a = 0.22 \text{ \AA}^{-2}$  for the coefficient of the exponential function in the Debye-Waller factor and thus found  $\tau_0 = 1.5 \cdot 10^{-12}$  sec. This result is apparently in good agreement with the data of [12] ( $a = 0.202 \text{ \AA}^{-2}$  and  $\tau_0 = 1.48 \cdot 10^{-12}$  sec), but it was shown in [12], on the basis of an account of the experimental data obtained for  $Q^2$  values of  $2.2 \text{ \AA}^{-2}$ , that the Oskotskii model is more suitable. This model incorporates two diffusion coefficients:  $D_0$ , which characterizes the motion of the atom along with its surroundings, and  $D_1$ , which characterizes the jumps of the atom. These coefficients are related to the classical diffusion coefficient by  $D_0\tau_0 + D_1\tau_1 = D(\tau_0 + \tau_1)$ . On the basis of this model, and retaining the assumption  $\tau_1 \ll \tau_0$ , we find an expression for the half-width of the quasielastic peak which depends on two parameters [13]:  $\tau_0$  and  $f = (D_1\tau_1/D\tau_0)$ . The best agreement with experiment is found with  $\tau_0 = 3.94 \cdot 10^{-12}$  sec and  $f = 0.5$ . As Fig. 3 shows, roughly the same agreement can be found on the basis of the Egelstaff-Schofield model [11], if the parameter  $c$  is assigned a value of  $1.47 \cdot 10^{-12}$  sec in the calculation of the half-width of the elastic peak.

The sensitivity of the calculated half-width of the quasielastic peak to the value of the free parameter differs in the various models. For  $Q = 1.3 \text{ \AA}^{-1}$  in the Singwi-Sjolander model, e.g., the value  $\Delta E$  approximately doubles as  $\tau_0$  is halved (reduced from  $2 \cdot 10^{-12}$  sec to  $1 \cdot 10^{-12}$  sec), while a halving of the parameter  $c$  (a change from  $1.87 \cdot 10^{-12}$  sec to  $0.99 \cdot 10^{-12}$  sec) in the Egelstaff-Schofield model is accompanied by a  $\Delta E$  increase of only 10%. For a given  $Q$ , of course, these figures are governed by the choice of liquid as well as by the choice of model. Nevertheless these results illustrate the difficulties which arise in trying to determine how the various models agree with experiment and in determining the values of the free parameter.

These difficulties can be avoided in part by careful experiments. A better resolution is required in order to distinguish the purely quasielastic component of the scattered-neutron spectrum. If the spectral width of the incident beam were reduced to a value in the range  $10^{-5}$ – $10^{-7}$  eV, the ratio of the resolution to the width of the quasielastic peak could be kept below a few percent, even at small  $Q$  (smaller than  $0.2 \text{ \AA}^{-1}$ ). Of course, it is also necessary to achieve a good angular resolution, especially at small  $Q$ . From an analysis of the data in Fig. 1 we see that a desirable value of the ratio  $\Delta Q/Q$  is on the order of a few percent.

tion of Randolph's data from a straight line corresponding to continuous diffusion can be attributed to experimental error (the relatively large spectral width of the incident beam and the uncertainty in  $\Delta Q$ ). It would be interesting to carry out more accurate measurements of the quasielastic scattering at small  $Q$  ( $Q < 0.5 \text{ \AA}^{-1}$ ). As has been shown [13] on the basis of [17], in a measurement of the diffusion coefficient the observation time must be much longer than the time over which a velocity correlation is displayed. This circumstance fundamentally restricts that region of  $(\hbar\omega - Q)$  space in which classical diffusion can be observed on the basis of neutron scattering.

At large  $Q$ , as Fig. 3 shows, the various models for microscopic diffusion lead to results in equal (qualitative) agreement with experiment. The functions  $\Delta E(Q^2)$  corresponding to all these models depend on several parameters. It was shown in [15] that for a given  $Q$  the quantity  $\Delta E$  is governed by the classical diffusion coefficient, the Debye-Waller factor, the period  $\tau_0$  of the oscillation of an atom with respect to its equilibrium center, and the time interval  $\tau_1$  between the jumps of this center. The



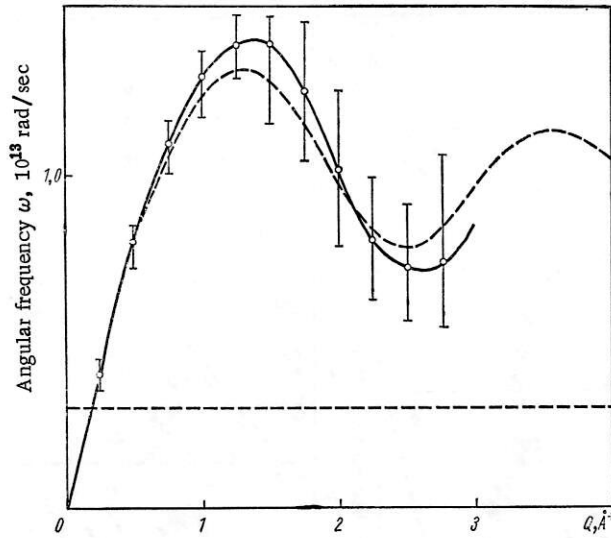


Fig. 4. The  $\omega(Q)$  curve for liquid argon [19]. Solid curve) Calculated from Eq. (3); broken curve) approximate calculation.

### 3. INELASTIC SCATTERING

In an analysis of the inelastic component of the spectrum of neutrons scattered in simple liquids, collective motion is naturally treated in the same manner as in a crystal. One of the first systematic studies of this question was that made by Larsson et al. for liquid aluminum [18]. Since then, much experimental information has been accumulated, and real progress has been made. The results reported by Hubbard and Beeby [19] are particularly interesting; they introduced the concept of the response function of the system in an analysis of the collective motion of a system of atoms. The linear-response function  $K$  describes the change in the density of the system under the influence of the external field. This function represents the generalized susceptibility of the system and, since it is a function of the frequency of the external field, has singularities corresponding to the collective-oscillation frequencies. Working from phonon theory, Hubbard and Beeby first carried out calculations for a disordered steady-state atomic system and then generalized these results to the dynamic case. The basic relation which relates the response function to the neutron-scattering function  $S(Q, \omega)$  is

$$S(Q, \omega) = \frac{1}{\pi\sigma} \cdot \frac{\hbar\omega}{1 - e^{-\hbar\omega/kT}} \cdot \frac{K''(Q, \omega)}{\omega}, \quad (1)$$

where  $\sigma$  is the number of atoms per unit volume,  $K''$  is the imaginary part of the function  $K$ ,  $\hbar\omega = E_0 - E$ , and  $k$  is the Boltzmann constant.

This response function of the system is expressed in terms of the function  $q(Q, \omega)$  and the frequency  $\omega_Q$ , characteristic of the system and dependent on  $Q$ :

$$K(Q, \omega) = -\frac{\sigma Q^2}{m} \cdot \frac{q(Q, \omega)}{1 + \omega_Q^2 q(Q, \omega)}, \quad (2)$$

where  $m$  is the atomic mass.

In order to use Eq. (2) to study a given liquid we must determine  $q(Q, \omega)$  and  $\omega_Q$ . We let  $v(r)$  be the binary potential for a system of  $N$  atoms making up the physical system. If we assume that the reaction of the system to a small external potential is governed primarily by the longitudinal motion, we find [19]

$$\omega_Q^2 = \frac{\sigma}{m} \int \frac{\partial^2 v}{\partial z^2} g(r) (1 - \cos Qz) dr, \quad (3)$$

where  $\sigma g(r)$  is the distribution of atomic pairs [ $g(r)$  tends to unity as  $r \rightarrow \infty$ ].

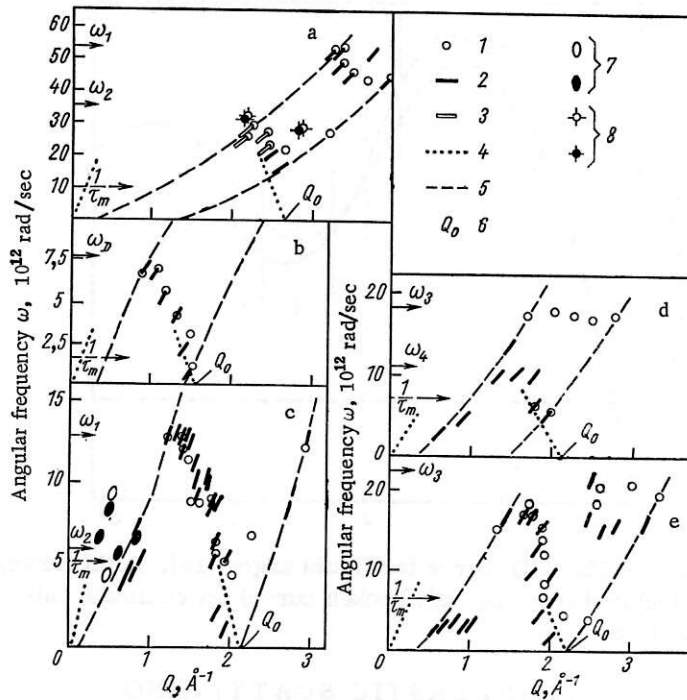


Fig. 5. Experimental data on  $\omega(Q)$  for several metals in the solid (polycrystalline) and liquid states [20]. a) Aluminum, liquid at 710°C and solid at 607°C; b) rubidium, liquid at 77°C and solid at 23°C; c) lead, liquid at 360°C and solid at 310°C; d) bismuth, liquid at 289°C and solid at 250°C; e) tin, liquid at 258°C and solid at 220°C. 1) Peak in solid; 2) peak in liquid; 3) unidentified peak in liquid; 4) sound velocity in liquid; 5) boundaries of the observation region; 6) principal maximum in the structure factors; 7) data of Dorner et al.; 8) data of Larson et al.  $\omega_1$ ) Longitudinal-oscillation peak;  $\omega_2$ ) transverse-oscillation peak;  $\omega_3$ ) optical-oscillation frequency;  $\omega_4$ ) acoustic-oscillation frequency;  $\omega_D$ ) Debye frequency.

The function  $q(Q, \omega)$  is found from

$$q(Q, \omega) = \int_0^\infty dt \int d\mathbf{r} g_s(\mathbf{r}, t) e^{-i\mathbf{Q}\mathbf{r} + i\omega t}, \quad (4)$$

where  $g_s(\mathbf{r}, t)$  is the autocorrelation function.

In order to apply this method to the inelastic scattering of neutrons in simple liquids we must determine  $g(\mathbf{r})$ ; i.e., we must measure  $S(Q)$  for elastic coherent scattering as well as the function  $g_s(\mathbf{r}, t)$ . Lacking the necessary experimental data, Hubbard and Beeby carried out approximate calculations of  $\omega_Q$  and  $q(Q, \omega)$ ; it is more difficult to evaluate the accuracy of the approximate calculation in the latter case. The results found for the functions  $\omega_Q$  were more convincing.

Analysis of the product  $(\partial^2 v / \partial z^2)g(\mathbf{r})$ , where  $v$  is the Lennard-Jones potential and  $g(\mathbf{r})$  is an empirical quantity, shows that it must have a maximum at some distance  $r_0$ , i.e., that this product can be approximated by a function  $A\delta(\mathbf{r} - \mathbf{r}_0)$ . Figure 4 shows calculated  $\omega(Q)$  curves [19] for liquid argon. These calculations were carried out on the basis of expression (3) and the approximation mentioned above. Comparison of Fig. 4 with Fig. 5 from [20] which shows experimental values of  $\omega(Q)$  for several liquid metals, reveals that the theoretical results of Hubbard and Beeby best reflect the dispersion curves for simple liquids.

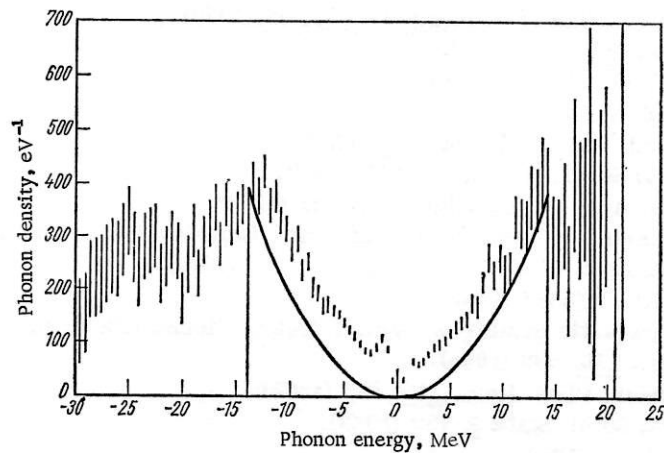


Fig. 6. Phonon spectrum of liquid sodium at 102°C. Solid curve) Debye spectrum at  $\theta = 170^\circ$ ,  $E_{\max} = 14$  MeV.

In a study of the collective motion in liquid lead [21, 22], an attempt was made to explain the dispersion curve by extending hydrodynamic theory to the range of relatively high frequencies. A qualitative agreement was found only for  $Q < 2 \text{ \AA}^{-1}$ . It would of course be interesting to compare these results with those based on the theory of [19]. In particular, it would be interesting to see the results of a more careful study of the temperature dependence of the collective motion.

In a study of liquid sodium, Randolph [13] analyzed the spectral component due to inelastic incoherent scattering from neutrons, assuming the collective motion of the liquid to be analogous to that in a cubic crystal. Using the differential effective cross section found in the one-phonon approximation [23], Randolph found the phonon spectrum for liquid sodium. His data agree well with Debye spectrum for  $\theta = 162^\circ\text{K}$  (this value is chosen on the basis of an analysis of the dispersion relations for solid sodium; see Fig. 6 [13]). This result is of only a qualitative nature because of the experimental conditions (in particular, because of multiple scattering and the coherent-scattering contribution).

Cocking [12] carried out a more detailed analysis of the phonon spectrum, comparing the experimental data with data found from the spectrum characteristic of solid sodium and with data from the Egelstaff-Schofield model for the liquid state. In this manner he was able to describe the phonon spectrum characteristic of liquid sodium.

Starting from the same experimental data, we can determine the spectral density corresponding to the velocity-correlation function [1, 11]:

$$\tilde{Z}(\omega) = \frac{\omega^2 S_s(Q, \omega)}{Q^2} \Big|_{Q \rightarrow 0}. \quad (5)$$

Egelstaff pointed out that by analyzing this quantity one could extract information about the interatomic potential. Comparison of  $\tilde{Z}(\omega)$  with  $v(r)$  (with an oscillatory potential used for liquid sodium [24, 25] and the 6-12 potential used for liquid argon [26]) allowed him to find that the  $\tilde{Z}(\omega)$  maximum was related to the shape of the potential well.

The results found from the study of liquid sodium show that a careful study of the region near the origin in  $(\hbar\omega - Q)$  space may reveal the characteristic features of collective motion in liquid. It would apparently be particularly interesting to study the temperature dependence of the phonon spectrum and the function  $\tilde{Z}(\omega)$  for the entire temperature range from the melting point to the boiling point.

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