

LIQUID DYNAMICS AND INELASTIC SCATTERING OF NEUTRONS

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Abstract

The energy transfers in one collision between a neutron and a liquid are computed by a method of moments. It is shown that for large momentum transfers a perfect gas model is correct. For small momentum transfers a macroscopic description of the density fluctuations in the liquid is applicable. It is in the intermediate region (where diffraction peaks are observed) that the method of moments is most useful. These different experimental situations are discussed for liquids where recoil and quantum effects are negligible, and numerical results are given for argon. An approximation for the so called autocorrelation function, valid for both long and short time scales and all distances, is also presented.

1. *Introduction.* Microscopic dynamics of liquids are very poorly known at the present time. Apart from neutron scattering experiments which have been started quite recently ¹⁾²⁾³⁾ the first information came from optical measurements on the Brillouin doublet ⁴⁾⁵⁾⁶⁾, which confirmed the existence of sound waves in the liquid. Further information was provided by dielectric relaxation ⁷⁾ and nuclear magnetic resonance ⁸⁾, experiments leading to a diffusion constant and giving its variation with temperature. Studies on isotopic mixtures give a similar information.

It is very important to notice that in most of these experiments the relevant time scale is *extremely long* when compared to a typical time interval in the liquid motion.

$$\tau \cong a[M/k_B T]^{\frac{1}{2}} = 10^{-13} \text{ to } 10^{-12} \text{ sec.}$$

(M is the atomic mass, a an average interatomic distance. We have assumed a monatomic classical liquid). The characteristic time for optical experiments with an ingoing radiation of wavelength λ is approximately $\lambda/s \sim 10^{-10}$ sec (s = sound velocity in the liquid). In dielectric or NMR measurements, periods are of order 10^{-8} sec. Also, the "hopping time" for self diffusion effects is something like $\tau e^{\Delta E/k_B T} \gg \tau$ (ΔE is the activation energy for diffusion).

The situation is entirely different when we come to the inelastic scattering of slow neutrons by liquids, because τ is comparable to \hbar/E_0 (where E_0

is the energy of the incoming neutron). Neutrons are sensitive to the detailed microscopic behaviour of the atomic motions. Such a situation cannot be described correctly by a simple extrapolation of the experimental results mentioned above which are related with a longer time scale. This, as we shall see, is a serious objection to the brownian motion or diffusion-type approximations which have been proposed recently⁹⁾ to describe the neutron inelastic scattering. Our method, here, will be to perform a rigorous calculation of the moments of a distribution function which is simply related to the energy spectrum of the outgoing neutrons. This use of moments has been initiated by Van Vleck in the field of magnetic resonance¹⁰⁾. It is extremely valuable for all cooperative systems which show a strong disorder. We applied it recently to the magnetic scattering of neutrons by an assembly of spins coupled by exchange forces¹¹⁾. For liquids, the relevant formulas have been given in a 1943 paper by Yvon¹²⁾. The results are given in terms of:

- a) – the potential between atoms
- b) – the pair distribution function (as measured by X-rays).

On the other hand there are two drawbacks. First, it is sometimes not enough to know a distribution function only through its first moments. Second, we are not always able to relate our results to a single experimental quantity such as a self diffusion coefficient. (We shall see how these difficulties may be by-passed in some simple situations). Apart from the basic information on the nature of the liquid state, the knowledge of the moments of the energy transferred from neutron to liquid in one collision, might be of interest for reactor technology problems, where one is mainly dealing with averages.

2. *Classical monatomic liquids.* We consider now a single collision of a neutron with a mono-atomic liquid.

Let $\hbar\mathbf{k}_0$ and $\hbar\mathbf{k}_1$ be the momentum of the incoming and outgoing neutrons, respectively. Two important quantities that come into play are

- a) the energy transferred from the neutron to the liquid during the collision

$$\hbar\omega = (\hbar^2/2m)(k_0^2 - k_1^2) \quad (m = \text{neutron mass}) \quad (1)$$

and b) the momentum transfer

$$\hbar\boldsymbol{\kappa} = \hbar(\mathbf{k}_0 - \mathbf{k}_1) \quad (2)$$

The differential scattering cross section for coherent scattering in a solid angle $d\Omega$ and an energy interval $\hbar d\omega$ is given by the Van Hove formula¹³⁾

$$\frac{d^2\sigma_{coh}}{d\Omega d\omega} = a^2_{coh} \frac{k_1}{k_0} \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle q_{-\boldsymbol{\kappa}}(0) q_{\boldsymbol{\kappa}}(t) \rangle \quad (3)$$

Here a_{coh} is the coherent scattering length, q_κ is the κ . Fourier component of the density in the liquid.

$$q_\kappa = \sum_i e^{i\kappa \cdot R_i} \tag{4}$$

and the $\langle \ \rangle$ symbol denotes a thermal average on the configurations and velocities in the liquid (with no neutrons present).

We see that the differential coherent cross section essentially gives information on the time correlation function of q_κ . Define:

$$p_\kappa(\omega) = \frac{1}{2\pi N} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle q_{-\kappa}(0) q_\kappa(t) \rangle \tag{5}$$

(N is the number of atoms in the liquid).

This function contains all the statistical information we need. Considering κ as a parameter, we call $p_\kappa(\omega)$ the distribution function of the ω 's. This is *not*, in general, identical with the energy spectrum of the outgoing neutrons for fixed scattering angle φ , because κ is itself a function of ω in such experiments:

$$\kappa = 2^{\frac{1}{2}} k_0 \left[1 + \frac{m\omega}{\hbar k_0^2} - \cos \varphi \left(1 + \frac{2m\omega}{\hbar k_0^2} \right)^{\frac{1}{2}} \right] \tag{6}$$

However, for crystal spectrometer studies, and liquids with atomic mass higher than 1, the energy transfer are much smaller than the energy of the incoming neutrons; $m\omega/\hbar k_0^2$ may be safely neglected in (6). κ is then fixed for a fixed scattering angle, and the observed energy spectrum is directly proportional to $p_{2k_0 \sin \varphi/2}(\omega)$. In experiments with very light liquids, or with sub-thermal neutrons (as is usually the case with velocity selectors), a numerical computation using (1) and (6) is necessary to go from the theoretical $p_\kappa(\omega)$ to the expected energy spectrum at fixed angle.

We now turn to the case of incoherent scattering, where the differential cross section is given by

$$\frac{d^2\sigma_{inc}}{d\Omega d\omega} = Na^2_{inc} \frac{k_1}{k_0} \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle e^{-i\kappa \cdot R_1(0)} e^{i\kappa \cdot R_1(t)} \rangle \tag{7}$$

R_1 is the coordinate of an arbitrary atom in the liquid.

Again we introduce a distribution function

$$r_\kappa(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle e^{-i\kappa \cdot R_1(0)} e^{i\kappa \cdot R_1(t)} \rangle \tag{8}$$

The total area of the distribution functions $p_\kappa(\omega)$ and $r_\kappa(\omega)$ are well known

$$S(\kappa) \equiv \int p_\kappa(\omega) d\omega = 1/N \langle q_{-\kappa}(0) q_\kappa(0) \rangle \tag{9}$$

$$= (4\pi/\kappa) \int_0^\infty R dR g(R) \sin(\kappa R) \tag{10}$$

where $g(R)$ is the pair density function.

$$\int r_{\kappa}(\omega) d\omega = 1. \quad (11)$$

We now show that the higher moments of these distribution functions can also be computed. Let us put:

$$\overline{\omega^n}_{coh}(\kappa) = \frac{\int \omega^n \phi_{\kappa}(\omega) d\omega}{\int \phi_{\kappa}(\omega) d\omega} \quad (12)$$

$$\overline{\omega^n}_{inc}(\kappa) = \frac{\int \omega^n r_{\kappa}(\omega) d\omega}{\int r_{\kappa}(\omega) d\omega} \quad (13)$$

A well-known formula on Fourier transforms gives:

$$\overline{\omega^n}_{coh}(\kappa) = (-i)^n \frac{1}{NS(\kappa)} \langle q_{-\kappa} \frac{d^n}{dt^n} q_{\kappa} \rangle \quad (14)$$

$$\overline{\omega^n}_{inc}(\kappa) = (-i)^n \langle e^{-i\kappa \cdot R_1} \frac{d^n}{dt^n} e^{i\kappa \cdot R_1} \rangle \quad (15)$$

The important feature in these equations is that all quantities in the thermal average bracket are to be taken at the same time, so that they may be computed exactly through a repeated use of the equations of motion. These equations are quantum mechanical. However, it is correct to use their classical form provided that the following assumptions are satisfied:

a) – the recoil of the atoms is negligible. If M is the atomic mass and T_0 the temperature of the incident neutrons, this condition may be approximated by

$$mT_0/MT \ll 1$$

b) – quantum effects in the liquid motion are small.

A first condition here is that the zero point energy ($\propto \hbar^2/Ma^2$) be small when compared to the average potential energy. This is equivalent to consideration of the De Boer parameter¹⁴⁾. London¹⁵⁾ has shown that, when this condition is *not* satisfied, the liquid configuration is the most stable even at 0°K, so that ³He and ⁴He are the only outstanding examples. A second condition for classical motion would be $\hbar^2/Ma^2 \ll k_B T$. In practice, when the first condition is satisfied, the second is also satisfied in general.

We now restrict ourselves to situations where assumptions a) and b) are correct, and compute the moments in the classical approximation. It is first to be noticed that all moments of odd order vanish. The second order moment for coherent scattering is:

$$\begin{aligned} \overline{\omega^2}_{coh}(\kappa) &= -\frac{1}{NS(\kappa)} \langle q_{-\kappa} \frac{d^2}{dt^2} q_{\kappa} \rangle \\ &= \frac{1}{NS(\kappa)} \left\langle \left| \frac{d}{dt} q_{\kappa} \right|^2 \right\rangle \\ &= \frac{\kappa^2}{NS(\kappa)} \sum_{ij} \left\langle \frac{dx_i}{dt} \frac{dx_j}{dt} e^{i\kappa(x_j - x_i)} \right\rangle \end{aligned} \quad (16)$$

(where we have taken the x axis in the direction of K). The velocities $v_i = dx_i/dt$ of different atoms are uncorrelated, and the average squares of the velocities are given by the Maxwell law, so that

$$\overline{\omega^2_{coh}} = \kappa^2 k_B T / MS(\kappa) \tag{17}$$

Similarly:

$$\overline{\omega^2_{inc}}(\kappa) = \kappa^2 (k_B T / M) \tag{18}$$

$$\begin{aligned} \overline{\omega^4_{coh}} &= \frac{1}{NS(\kappa)} \langle q_{-\kappa} \frac{d^4}{dt^4} q_{\kappa} \rangle \\ &= \frac{1}{NS(\kappa)} \left\langle \left| \frac{d^2}{dt^2} q_{\kappa} \right|^2 \right\rangle \\ &= \frac{1}{NS(\kappa)} \left[\kappa^4 \sum_{ij} \langle v_i^2 v_j^2 e^{i\kappa x_{ij}} \rangle + \frac{i\kappa^3}{M^2} \sum_{ij} \langle v_j^2 \frac{\partial U}{\partial x_i} e^{i\kappa x_{ij}} - v_i^2 \frac{\partial U}{\partial x_j} e^{i\kappa x_{ij}} \rangle + \right. \\ &\quad \left. + \frac{\kappa^2}{M^2} \sum_{ij} \left\langle \frac{\partial U}{\partial x_i} \frac{\partial U}{\partial x_j} e^{i\kappa x_{ij}} \right\rangle \right] \tag{20} \end{aligned}$$

($x_{ij} = x_j - x_i$)

Here $U(\mathbf{R}_1, \mathbf{R}_2 \dots \mathbf{R}_N)$ is the potential energy of the N atoms. The probability of a configuration of the N atoms is proportional to $e^{-\mu/k_B T}$, so that, if $F(R_1 \dots R_N)$ is any regular function

$$\langle F(\partial U / \partial x_i) \rangle = k_B T \langle \partial F / \partial x_i \rangle \tag{21}$$

as may be seen through an integration by parts. This remark of Yvon¹²⁾ greatly simplifies the above expression for $\overline{\omega^4_{coh}}$, which finally reads:

$$\overline{\omega^4_{coh}}(\kappa) = \frac{1}{s(\kappa)} \left[3\kappa^4 \left(\frac{k_B T}{M} \right)^2 + \kappa^2 \frac{k_B T}{MN} \sum_{ij} \left\langle \frac{\partial^2 U}{\partial x_i \partial x_j} e^{i\kappa x_{ij}} \right\rangle \right] \tag{22}$$

We get in the same way

$$\overline{\omega^4_{inc}}(\kappa) = 3\kappa^4 (k_B T / M)^2 + \kappa^2 (k_B T / M^2) \langle \partial^2 U / \partial x_1^2 \rangle \tag{23}$$

If we further assume that the potential energy U is of the form

$$U = \sum_{i < j} V(\mathbf{R}_{ij}) \tag{24}$$

we may express the moments in terms of this V function and of the pair density function $g(R)$

$$\overline{\omega^4_{coh}}(\kappa) = \frac{\kappa^4 k_B T}{M^2 S(\kappa)} \left[3k_B T + \int d\mathbf{R} g(R) \frac{1 - \cos(\kappa x)}{\kappa^2} \frac{\partial^2 V}{\partial x^2} \right] \tag{25}$$

$$\overline{\omega^4_{inc}}(\kappa) = \frac{\kappa^4 k_B T}{M^2} \left[3k_B T + \int d\mathbf{R} g(R) \frac{1}{\kappa^2} \frac{\partial^2 V}{\partial x^2} \right] \tag{26}$$

These are the basic formulas which will be used in the following sections.

3. *Incoherent scattering.* We discuss first the distribution function $r_\kappa(\omega)$ for the *incoherent* part of the scattering, which is the simpler of the two. Its area is independent of K by (11) so that the total scattered intensity is essentially isotropic (apart from the effect of k_1/k_0 in the cross section formula). However, the moments do depend on κ . The second moment, which is given by (18) is independent of the potential energy function V : it has the same value in a real liquid as in a perfect gas at the same temperature and with the same atomic mass. At first sight, one could then be tempted to take for $r_\kappa(\omega)$ the perfect gas value which is (neglecting recoil):

$$r_\kappa(\omega)_{\text{perf. gas}} = \frac{1}{\kappa} \left[\frac{M}{2\pi k_B T} \right]^{\frac{1}{2}} \exp\left(\frac{-M\omega^2}{2\kappa^2 k_B T}\right) \quad (27)$$

This is not correct in general, as shown by the fourth moment. This fourth moment (26) may be written:

$$\overline{\omega^4}_{inc}(\kappa) = 3[\overline{\omega^2}_{inc}(\kappa)]^2 + \overline{\omega^2}_{inc}(\kappa)\Omega_0^2 \quad (28)$$

where we have introduced a characteristic frequency Ω_0 through:

$$M\Omega_0^2 = \int d\mathbf{R} g(R) \frac{\partial^2}{\partial x^2} V(R) \quad (29)$$

$$= \frac{4\pi}{3} \int_0^\infty R^2 dR g(R) \left[\frac{2}{R} \frac{\partial V}{\partial R} + \frac{\partial^2 V}{\partial R^2} \right] \quad (30)$$

Ω_0 is strongly temperature dependent because it is most sensitive to $g(R)$ in the region where $V(R)$ varies steeply.

1) - When κ is large, $\overline{\omega^2}_{inc}(\kappa)$ (which is proportional to κ^2) is larger than Ω_0^2 , and the second term on the right in (28) is negligible when compared to the first. The fourth moment is then what we expect for a gaussian $\overline{\omega^4} = 3[\overline{\omega^2}]^2$ and the perfect gas model is applicable.

2) - On the contrary, when κ gets small, the fourth moment is much larger than expected for a Gaussian curve; this means that the actual $r_\kappa(\omega)$ has large wings, and is indeed what we should find in terms of the diffusion model (this model is correct when one deals with small values of κ and small energy transfers; long distances and long time scale). We accordingly expect $r_\kappa(\omega)$ to be well described here by a Lorentz curve, as deduced from diffusion considerations⁹⁾:

$$r_\kappa(\omega) = \frac{1}{\pi} \frac{\Lambda\kappa^2}{\omega^2 + \Lambda^2\kappa^4} \quad (31)$$

It is to be noted, however, that the above shape is not correct far in the wings (short time scale region). In fact, it would predict infinite moments.

We now proceed to show that a more detailed model may be proposed, and fitted to the values of the moments over the whole range of κ values. It is.

in fact, a straightforward extension to liquids of a calculation by Anderson and Weiss¹⁶) on exchange narrowing.

We consider the Fourier transform of $r_\kappa(\omega)$

$$\rho_\kappa(t) = \int d\omega r_\kappa(\omega) e^{i\omega t} \tag{32}$$

$$= \langle e^{-i\kappa x_1(0)} e^{i\kappa x_1(t)} \rangle \tag{33}$$

Let $V_1(t)$ be the instantaneous velocity along the x axis of atom (1). At every instant v_1 is distributed according to a Gaussian probability law, and a well known theorem says that the same is true for

$$x_1(t) - x_1(0) = \int_0^t v_1(t') dt' \tag{34}$$

which is a sum of such variables. It is then easy to see that

$$\langle e^{i\kappa(x_1(t) - x_1(0))} \rangle = \exp\left(-\frac{1}{2}\kappa^2 \langle (x_1(t) - x_1(0))^2 \rangle\right) \tag{35}$$

and this may be written

$$\rho_\kappa(t) = \exp\left(-\kappa^2 \int_0^t dt' (t - t') \langle v_1(0) v_1(t') \rangle\right) \tag{36}$$

Up to now our formulas are rigorous for a classical system (fluid or solid). In a crystalline solid, the correlation function $\langle v_1(0) v_1(t) \rangle$ displays an oscillatory behaviour with decreasing amplitude. Such oscillations are much more strongly damped in the liquid phase. We shall use here the extreme approximation where the oscillations are completely neglected, and choose an approximate expression giving a smooth decrease. It then turns out that the final numerical results are rather insensitive to the analytical form chosen, provided that it gives the correct values for the moments of the distribution function. We take:

$$\langle v_1(0) v_1(t) \rangle = (k_B T/M) \exp\left(-\frac{1}{2}\Omega_0^2 t^2\right) \tag{37}$$

Ω_0^{-1} appears here as a correlation time for velocities in the liquid. Direct computation of the moments of r_κ using its Fourier transform as given by (36) and (37) shows that Ω_0 is identical with the earlier defined quantity (eq. 30).

The limiting behaviour of $\rho_\kappa(t)$ for large and small momentum transfers are easily shown to be

$$\rho_\kappa(t) = \exp\left(-\frac{1}{2}\overline{\omega^2}_{inc}(\kappa)t^2\right) \quad \Omega_0^2 \ll \overline{\omega^2}_{inc}(\kappa) \tag{38}$$

$$\rho_\kappa(t) = \exp\left(-\sqrt{\frac{\pi}{2}} \frac{\overline{\omega^2}_{inc}(\kappa)}{\Omega_0} t\right) \quad \Omega_0^2 \gg \overline{\omega^2}_{inc}(\kappa) \tag{39}$$

These are exactly the forms we expected from our preliminary discussion, as may be seen by taking the Fourier transforms of (27) and (31), provided we take:

$$A = (\pi/2)^{\frac{1}{2}} (k_B T/M\Omega_0) \tag{40}$$

Equations (40) and (30) give the self diffusion coefficient Λ in terms of the pair density function $g(R)$ and the potential energy function $V(R)$. Unfortunately it turns out that the latter is very poorly known in liquids where it has been measured, so that a direct comparison is not possible.

Still it is gratifying that the theory depends on one parameter Λ only, whose value may be obtained independently by making use of measured values of Λ and eq. (40).

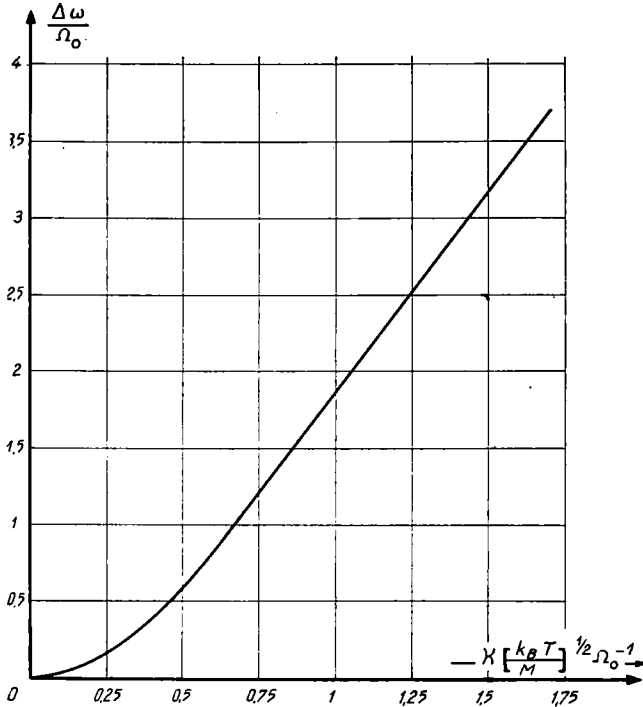


Fig. 1.

Apart from the limiting cases that we already considered, we may always calculate $r_\kappa(\omega)$ for intermediate values of κ by a numerical Fourier inversion of eq. (36) supplemented by (37). This is rather tedious, however, and we prefer to plot, as a function of κ , the width at half maximum $\Delta\omega(\kappa)$ for the distribution function $r_\kappa(\omega)$. To avoid dimensional factors we actually plot $\Delta\omega/\Omega_0$ as a function of $\kappa(k_B T/M)^{1/2} \Omega_0^{-1}$ (fig. 1). Numerical techniques relevant to this width problem are found in a paper by Anderson¹⁷.

4. *Coherent scattering.* The situation here is somewhat more complex because correlations between different atoms come into play.

We plot the "theoretical" values of $\overline{\omega^2_{coh}}$ and $\overline{\omega^4_{coh}}/3[\overline{\omega^2_{coh}}]^2$ for liquid argon at two typical temperatures along the vapour curve. We choose argon because

a) – the pair density function is rather well known; here we have used the values from X-ray scattering experiments by Eisenstein and Gingrich¹⁸.

b) – it is reasonable to take $V(R)$ as a Lennard Jones potential whose parameters are known through measurements in the gas phase:

$$V(R) = 475 k_B[(\sigma/R)^{12} - (\sigma/R)^6]$$

with $\sigma = 3.40 \text{ \AA}$.

The second moment (eq. 17) depends only on the pair density function $g(R)$ and its accuracy is comparable to that of the X-ray measurements. The fourth moment, however, is given by:

$$\frac{M^2 S(\kappa)}{\kappa^4 k_B T} \overline{\omega_{coh}^4}(\kappa) = 3k_B T + \frac{4\pi}{\kappa^2} \int_0^\infty R^2 dR g(R) \left[\frac{1}{R} \frac{\partial V}{\partial R} \left(1 - \frac{\sin(\kappa R)}{\kappa R} \right) + \left(\frac{\partial^2 V}{\partial R^2} - \frac{1}{R} \frac{\partial V}{\partial R} \right) \left(\frac{1}{3} - \frac{1}{\kappa^3 R^3} (2\kappa R \omega S(\kappa R) + (\kappa^2 R^2 - 2) \sin(\kappa R)) \right) \right] \quad (41)$$

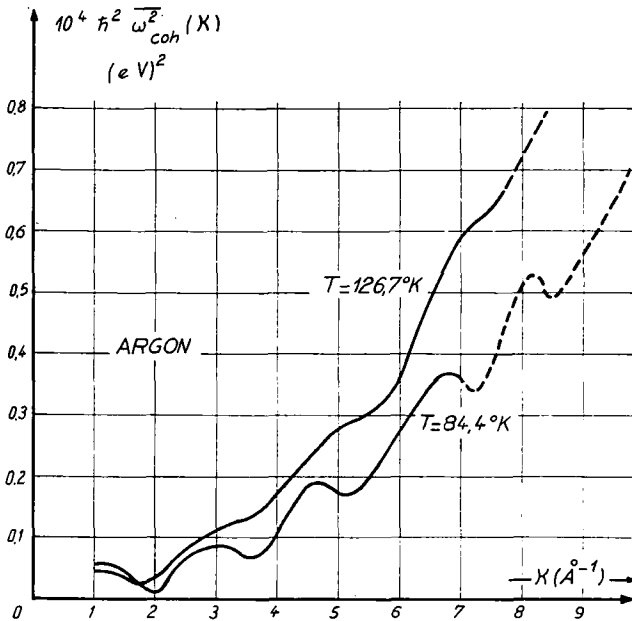


Fig. 2.

This integral is rather sensitive to the values of $g(R)$ around $R = \sigma$ and the accuracy of the fourth moment is accordingly lower, especially when we compare the values at two temperatures, $g(R)$ being strongly temperature dependent in that range of r values (We still think it better to use the experimental $g(R)$ rather than one of the various theoretical values proposed up to now).

The results are shown in figures 2 and 3. The second moment gives us a first indication on the width of the distribution function, and the ratio $\overline{\omega^4}/3[\overline{\omega^2}]^2$ (equal to unity for a Gaussian distribution) is a direct test for the perfect gas model, which predicts

$$P_{\kappa}(\omega)_{\text{perf. gas}} = \frac{1}{\kappa} \left[\frac{M}{2\pi k_B T} \right]^{\frac{1}{2}} \exp\left(-\frac{M\omega^2}{2\kappa^2 k_B T}\right) \quad (42)$$

(recoil of the atoms being always neglected).

Here again, we find different behaviours for the distribution function, depending on the values of the parameters.

1) - For $\kappa\sigma \gtrsim 2$, the perfect gas model is satisfactory. This is essentially the situation encountered by Pelah, Whittemore and MacReynolds³⁾ in their experiments on liquid lead, with neutrons of short wave length ($\sim 1\text{\AA}$) and large scattering angles. In such a situation, the line width is expected to vary as $T^{\frac{1}{2}}$.

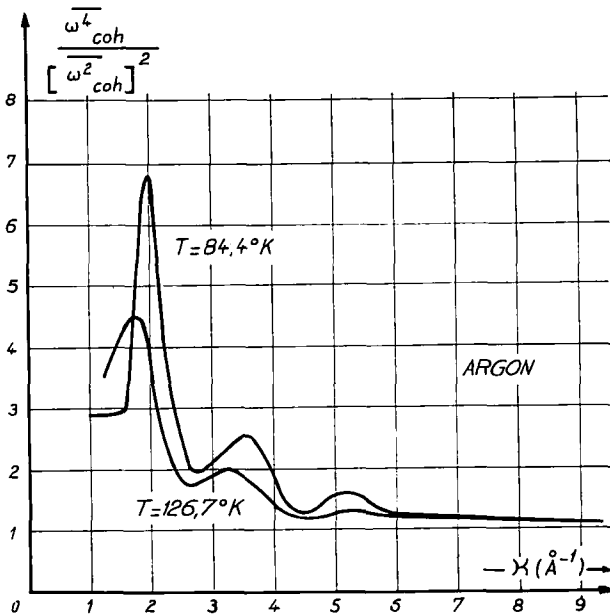


Fig. 3.

2) - For intermediate values of κ , the moments undergo strong oscillating variations. The major phenomenon is the following: when the value of κ corresponds to one of the diffraction peaks in the X ray pattern, $\overline{\omega^2}_{coh}$ becomes small and $\overline{\omega^4}_{coh}/3[\overline{\omega^2}_{coh}]^2$ becomes large. This means that for such κ values the distribution function is narrow and the shape is closer to a Lorentzian than to a Gaussian.

Unfortunately we cannot here supplement our moments calculation by a detailed picture of correlation functions; this would involve approximations more difficult to justify than in the incoherent case. For a numerical study of halfwidths, and "intermediate" or large values of κ we propose the following empirical procedure: define a frequency $\Omega(\kappa)$ by the relation

$$\overline{\omega^4}_{coh} = \overline{\omega^2}_{coh} [3\overline{\omega^2}_{coh} + \Omega^2]$$

This is a generalisation of the earlier introduced Ω_0 (and indeed $\Omega(\infty) = \Omega_0$). Substitute $[\overline{\omega^2}_{coh}]^{\frac{1}{2}}$ to $\kappa(k_B T/M)^{\frac{1}{2}}$ in the halfwidth plot (fig. 1) and $\Omega(\kappa)$ to Ω_0 . Comparison with other models suggests that the resulting $\Delta\omega/\Omega$ should be a good first approximation to the true values. Results of this approximation for Argon are shown on figure 4.

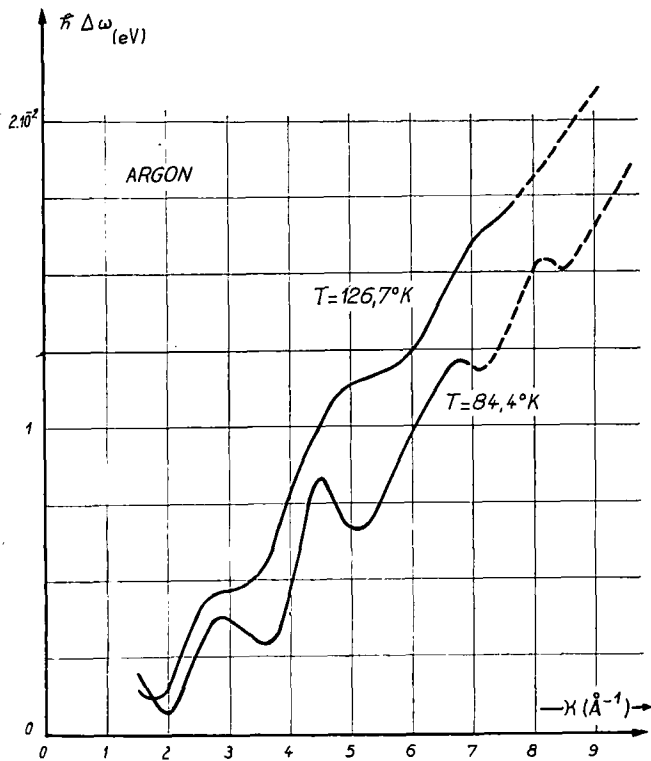


Fig. 4.

3) - For small κ values the moments have not been plotted in fig. 2 and 3 because of experimental inaccuracies in $S(\kappa)$. This region is essentially the same as the one covered by optical experiments. It is a difficult region for neutron scattering because the intensities are small (except near the critical point). On the other hand, it is a comfortable region for the theoretical physicist, because macroscopic considerations may be applied to these

long wave lengths and long time scale phenomena. From experiment and from a well known analysis by Landau, Placzek and Gross¹⁹⁾ one knows that the distribution function consists of *three lines*: one central line ($\omega = 0$) which is important mainly near the critical point, and two phonon lines ($\omega = \pm c\kappa$) on both sides (Brillouin doublet). In our approximation (neglecting recoil and quantum effects) both phonon lines have the same intensity $\frac{1}{2}I_1$. The ratio I_1/I_0 of the intensities in Brillouin doublet to the intensity in the central line may be deduced from our equations for the second moment.

$$\overline{\omega^2}_{coh} = \frac{I_1}{I_1 + I_0} c^2 \kappa^2 = \frac{\kappa^2 k_B T}{MS(\kappa)} \quad (43)$$

The low κ limit of $S(\kappa)$ is related to the isothermal compressibility $(\partial p/\partial n)_T$ by a well known relation

$$\lim_{\kappa \rightarrow 0} S(\kappa) = k_B T (\partial n/\partial p)_T \quad (44)$$

The sound velocity c is also known through the adiabatic compressibility $(\partial p/\partial n)_s$:

$$c^2 = (1/M)(\partial p/\partial n)_s. \quad (45)$$

We then get:

$$\frac{I_1}{I_0 + I_1} = \left(\frac{\partial p}{\partial n} \right)_T \left/ \left(\frac{\partial p}{\partial n} \right)_s \right. \quad (46)$$

This is precisely the value calculated by Gross¹⁹⁾ using a thermodynamic argument. In spite of this agreement we believe that a detailed test of the three line model by computation of the moments should take into account damping effects. These effects might be independently estimated by means of macroscopic equations for heat flow, mass flow and mechanical motion. Such a calculation has been undertaken by Butterworth and Marshall²⁰⁾ (We disagree, however, with their assumptions on the existence of transverse vibrations).

To conclude our remarks we may say that neutron experiments on coherent scatterers in that range of small κ values would essentially lead to a determination of the sound velocity, dispersion and attenuation. A study of the central line width would also provide a measurement of a heat transfer coefficient¹³⁾.

5). *Conclusions.* The most important fact is that the behaviour of the inelastic scattering essentially depends on the value of the momentum transfer

1) – for large κ values the perfect gas model is applicable both for coherent and incoherent scattering.

2) – for intermediate κ values and coherent scattering correlation effects between neighbouring atoms are important and often result in a strong narrowing of the distribution function.

3) – for small κ values the results are fundamentally different depending on whether the scattering is coherent (three lines, which reduce to the Brillouin doublet for temperatures well below T_c) or incoherent (one single Lorentzian line).

It is easier to make complete experimental investigation over the whole range of κ values with a crystal spectrometer equipment than with a velocity selector: in the latter case wave lengths are longer ($\sim 4\text{\AA}$) and even at large angles the κ values do not usually exceed the “intermediate” range.

We now turn to some remarks on more general situations:

1) – *diatomic liquids* – The formulas for the moments are heavier, and also interaction potentials are poorly known. We may however derive some simple, approximate results for the second moment.

For incoherent scattering, we still have:

$$\int r_\kappa(\omega) d\omega = 1 \quad (47)$$

$$\overline{\omega^2}_{inc}(\kappa) = \kappa^2 \langle |dx/dt|^2 \rangle \quad (48)$$

But this average square velocity is not simply equal to $k_B T/M$ (where M is the *atomic* mass). Also for coherent scattering, putting again

$$\langle q_\kappa q_{-\kappa} \rangle = NS(\kappa) \quad (49)$$

(where N is the number of atoms) we may write $\int p_\kappa(\omega) d\omega = S(\kappa)$ and

$$\overline{\omega^2}_{coh} = \frac{\kappa^2}{NS(\kappa)} \sum_{ij} \left\langle \frac{dx_i}{dt} \frac{dx_j}{dt} e^{ix_{ij}} \right\rangle \quad (50)$$

Here, in contrast with the monoatomic case, there exist velocity correlations between different atoms.

We still expect that these correlations are small, except for atoms belonging to the same molecule. These velocity correlations inside one molecule should be very nearly the same as in a perfect diatomic gas, where they may be computed by standard techniques of classical mechanics.

This leads to the following values

$$\overline{\omega^2}_{inc}(\kappa) = (5/6) \kappa^2 k_B T/M \quad (51)$$

$$\overline{\omega^2}_{coh}(\kappa) = \frac{\kappa^2 k_B T}{MS(\kappa)} \left[\frac{5}{6} + \frac{1}{2\xi^3} (2\xi \cos \xi + (\xi^2 - 2) \sin \xi) \right] \quad (52)$$

where $\xi = \kappa d$ and d is the atomic distance in the molecule. The derivation of (51) and (52) neglects vibrational modulations of d (which lead to small and easily separated corrections for thermal neutrons). Also the case of

nuclear spin correlations between the two atoms in the molecule (as in hydrogen) should be treated separately.

2) – *Amorphous solids* – Kinetics of amorphous media are very poorly known, except for very long wave length phenomena. The method of moments may prove very useful here: assume for instance that there are different atomic species, each atom being associated with a coherent scattering amplitude a_i (depending on the atomic species to which (i) belongs). We then have, for coherent scattering:

$$\frac{d^2\sigma_{coh}}{d\Omega d\omega} = \frac{k_1}{k_0} \frac{1}{2\pi} \int dt e^{-i\omega t} \sum_{ij} a_i a_j \langle e^{i\mathbf{x}_i(0)} e^{i\mathbf{x}_j(t)} \rangle \quad (53)$$

Formulas for the moments of order 0,2 and 4 may easily be derived: they are simple generalisations of equations (10), (17) and (22). The pair density functions and rigidity coefficients that come in might be directly estimated from simple models of the amorphous phase.

3) – *Reactor technology* – The formulas which have been developed up to now are obviously not suitable for thermalisation problems, since we neglected the moments of odd order in the distribution function. However, the information collected suggests that for incident neutron wave lengths shorter than say one half the average intermolecular distance, a good starting approximation should be provided by the perfect gas model for the corresponding (mono or polyatomic) molecules.

This statement should of course be refined by a more detailed analysis, especially for associated liquids such as water.

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