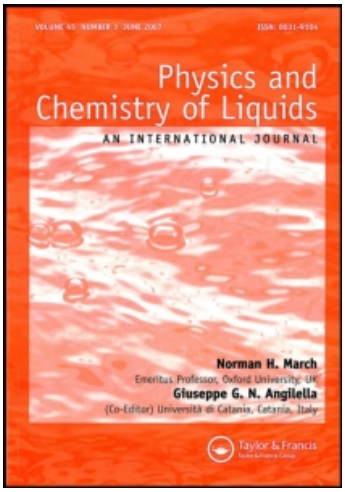

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Discussion of the Quasi Elastic Scattering of Neutrons in Incoherent Liquids

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Discussion of the Quasi Elastic Scattering of Neutrons in Incoherent Liquids

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Abstract—A critical discussion of the quasi-elastic scattering of neutrons by incoherent (hydrogenous) liquids is presented. Using the line shape expression a comparative discussion of several phenomenological models has been undertaken. Extension of the Singwi-Sjolander zero phonon expression, for the jump-diffusion model, so as to include the one phonon expression has also been given. For a delayed diffusion model a complete treatment of $S(K, \omega)$ is presented. Along the lines of the macroscopic diffusion cooling, a microscopic diffusion cooling effect in fluids is speculated.

Analysis of the Quasi Elastic Scattering of Neutrons in Hydrogenous Liquids

1. Introduction

In recent years extensive experimental information on the scattering of neutrons in hydrogenous liquids has been accumulated[1,2,3]. The analysis of these experiments requires the detailed understanding of the incoherent scattering of neutrons, as the hydrogen atom is the main scatterer. For the sake of simplicity one may divide the dynamical modes in hydrogenous liquids in three broad categories. These depend upon the magnitude of the energy transfer in the scattering process. First, the high energy transfer modes which involve the intramolecular vibrations. It is well known that the cold neutron scattering experiments do not provide the direct information about these modes. Due to the lack of neutron intensity the energy gain processes of the magnitude of these modes have not yet been studied. However these modes are presently being investigated by the energy loss method using the Rensselaer

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Polytechnic Institute linear accelerator.† Secondly, the medium energy transfer modes represented by the hindered rotations. The cold neutron scattering experiments have given the most valuable information about the structure of these modes. Thirdly, the low energy transfer modes, which cover the diffusive and hindered translational modes. The information about the diffusion of atoms in liquids has been obtained by analysing the quasi-elastic scattering of neutrons.

The analysis of the neutron scattering data in hydrogenous liquids would require the theory of the liquid state. At present there does not exist an adequate theory which can be employed in the analysis of these experiments. Attempts have been made by several authors to formulate phenomenological models to study the quasi-elastic scattering of neutrons. In this study we shall be primarily concerned with the critical discussion of this problem.

In section 2, we present a general formalism for studying the incoherent scattering of neutrons. The scattering law $S(K, \omega)$ is expressed in terms of a generalized diffusion coefficient $D(K, \omega)$. The latter is related to the response function corresponding to the fluctuations in the local density. This representation may be useful for a comparative study of several phenomenological models employed in the analysis of the quasi elastic scattering of neutrons.

We discuss in the third section three types of phenomenological models

(1) The diffusion model in the form applied by Vineyard.[4]

(2) The jump diffusion model of Singwi and Sjölander.[5] A variation of this model has been discussed by Oskotskii.[6] Rahman, Singwi and Sjölander[7] have formulated a stochastic model using the Langevin equation of motion to describe the damped harmonic vibrations and also diffusive modes.

(3) The single relaxation time models. Ruijgrok[8] and Kadanoff and Martin[9] modified the simple diffusion model so as to take into account the reversible character of the dynamical motion by introducing a single relaxation time. On the other hand, Nelkin and Ghatak[10] and Gibbs and Ferziger[11] introduced a single relaxation time tos-implify the collision integral in the linearised Boltzmann equation.

† See the recent measurements of G. J. Kirouac *et al*, *Nucl. Sci. Eng.* **25**, 300 (1966.)

In section 4, we present an extension of the Singwi-Sjölander expression for $S(K, \omega)$, so as to include the contribution of one phonon term explicitly. Singwi and Sjölander have treated only the zero phonon term. The section 5 deals with the treatment of a delayed diffusion model. We assume that for times greater than the correlation time t_c the diffusion process sets in. For times smaller than t_c we have solid like behavior.

An attempt has also been made to present a qualitative discussion of the temperature dependent quasi elastic scattering results in terms of the diffusion cooling phenomenon on a microscopic scale.

2. Neutron Scattering Formalism

According to Van Hove[12] the scattering law, $S(K, \omega)$, a function of momentum transfer $\hbar \underline{K}$ and energy transfer $\hbar\omega$ in the neutron scattering process, is completely determined by the dynamics of atomic motions in the system under consideration. For an incoherent scatterer, such as a hydrogenous system, we write $S(K, \omega)$ in the form of the Fourier transform of the intermediate scattering function, $F_s(K, t)$.

$$S(K, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \exp - i\omega t \, F_s(K, t) \, dt \tag{1}$$

and

$$F_s(K, t) = \langle \exp - i\underline{K} \cdot \underline{R}(0) \exp i\underline{K} \cdot \underline{R}(t) \rangle . \tag{2}$$

$\underline{R}(t)$ is the position vector of the scattering nucleus at time t in the Heisenberg representation, that is

$$R(t) = \exp iHt \, R(0) \exp - iHt . \tag{3}$$

In the above equation H represents the Hamiltionian of the system. The bracket $\langle \ \rangle$ in the expression of $F_s(K, t)$ represents the quantum statistical average. For the harmonic vibrations in a crystal $S(K, \omega)$ has been extensively discussed in the literature. See the recent review article of Waller.[13] One may also refer to the review article of Glauber[14] for the theory of neutron scattering by statistical media—gases and liquids.

In this study we shall express $S(K, \omega)$ in the form given by Zwanzig[15] and Kadanoff and Martin.[9] We adopt the notation of Zwanzig.

Let us define the Fourier transform (in space) of the density function.

$$\varrho(\underline{K}, t) = \exp i\underline{K} \cdot \underline{R}(t) . \tag{4}$$

Therefore,

$$S(K, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \exp - i\omega t \langle \varrho(-\underline{K}, 0)\, \varrho(\underline{K}, t) \rangle\, dt. \tag{5}$$

After taking time derivatives, we obtain

$$\omega^2 S(K, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \exp - i\omega t \langle \dot{\varrho}(-K, 0)\, \dot{\varrho}(\underline{K}, t) \rangle\, dt. \tag{6}$$

Derivation of the above expression depends upon the application of the following identity for the operators A and B based upon the time invariance property.

$$\langle A(-\underline{K}, \alpha)\, B(\underline{K}, \beta) \rangle = \langle A(-\underline{K}, \alpha + \gamma)\, B(\underline{K}, \beta + \gamma) \rangle. \tag{7}$$

From Eq. (6) one obtains the exact result for the second energy transfer moment.

$$\langle \omega^2 \rangle = \langle \dot{\varrho}(-\underline{K}, 0)\, \dot{\varrho}(\underline{K}, 0) \rangle. \tag{8}$$

We shall now express $S(K, \omega)$ in terms of the generalized diffusion coefficient tensor $D(K, \omega)$. From the law of the conservation of current density or the equation of continuity, we obtain

$$\dot{\varrho}(\underline{K}; t) = i\underline{K} \cdot \underline{j}(\underline{K}, t). \tag{9}$$

$\underline{j}(\underline{K}, t)$ is the Fourier transformed current density. Therefore,

$$S(K, \omega) = \frac{1}{2\pi\omega^2} \int_{-\infty}^{+\infty} \exp - i\omega t \langle \underline{K} \cdot \underline{j}(-\underline{K}, 0)\, \underline{j}(\underline{K}, t) \cdot \underline{K} \rangle\, dt. \tag{10}$$

The above representation is an alternate form of expressing $S(K, \omega)$.

Let us define the components of the diffusion coefficient tensor following Kubo[16] with $\beta = \dfrac{1}{kT}$.

$$D_{\mu\nu}(K, \omega) = \frac{1}{\beta} \int_0^{\infty} \exp - i\omega t \int_0^{\beta} \langle j_\mu(-\underline{K}, -i\hbar\lambda)\, j_\nu(\underline{K}, t) \rangle\, d\lambda\, dt. \tag{11}$$

The above expression is the generalization of the well known result for the diffusion coefficient which is obtained by taking the limit of $D_{\mu\nu}(K, \omega)$ for $K \to 0$ and $\omega \to 0$.

Let us write

$$D_{\mu\nu}(K, \omega) = \frac{1}{\beta} \int_0^\infty \exp - i\omega t \, \varphi_{\mu\nu}(K, t) \, dt. \tag{12}$$

The response function $\varphi_{\mu\nu}(K, t)$ is the λ-integral of Eq. (11). As $\varphi_{\mu\nu}(\underline{K}, t) = \varphi^*_{\mu\nu}(\underline{K}, -t)$ due to the invariance of the Heisenberg equation of motion under the transformation $t \to -t$ and $i \to -i$, therefore, we obtain following Kubo or Montroll.[17]

$$\mathrm{Re}\, D_{\mu\nu}(K, \omega) = \frac{(1 - \exp - \beta\omega\hbar)}{2\beta\hbar\omega} \int_{-\infty}^{+\infty} \exp - i\omega t \langle j_\mu(-\underline{K}, 0) \, j_\nu(\underline{K}, t)\rangle \, dt. \tag{13}$$

From Eqs. (10) and (13) follows

$$S(K, \omega) = \frac{\beta\hbar}{\pi\omega} \left[\frac{\underline{\underline{K}} \cdot \mathrm{Re}\, \underline{\underline{D}}(\underline{K}, \omega) \cdot \underline{\underline{K}}}{(1 - \exp - \beta\omega\hbar)} \right]. \tag{14}$$

Alternatively, one may also express $S(K, \omega)$ in terms of Im $A(K, \omega)$— the Fourier transform of Im $G(\underline{r}, t)$.

$$S(K, \omega) = \left(1 + \mathrm{Coth} \frac{\beta}{2} \omega\hbar\right) \mathrm{Im}\, A(K, \omega). \tag{15}$$

The above expression is a consequence of the following detailed balance condition

$$S(K, \omega) = \exp \beta\hbar\omega \, S(-K, -\omega) \tag{16}$$

which implies a definite connection between real and imaginary parts of the correlation function.

In the generalized case this relation constitutes the Fluctuation—dissipation theorem of the irreversible statistical mechanics. See Schofield[18], Glauber[14] and others.

According to Van Hove[19], Im $A(K, \omega)$ is the response to the fluctuations in the density $n(r, t)$ of the system caused by the transfer of momentum by a neutron during the scattering process. These fluctuations get dissipated in different dynamical modes. Mathematically,

$$\mathrm{Im}\, A(K, \omega) = \frac{1}{2\pi} \int d\underline{r} \, dt \exp i(\underline{K} \cdot \underline{r} - \omega t) \, \mathrm{Im}\, G(r, t). \tag{17}$$

$$n(r, t) = \varrho_0 - \left(\frac{2\pi a h^2}{m}\right) i\varrho_0 \int_{-\infty}^{t} dt' \, \mathrm{Im}\, G(r - r_t; t - t'). \tag{18}$$

ϱ_0 is the equilibrium density and the second term describes the fluctuations from the equilibrium value.

Ruijgork[8] and Egelstaff[20] have employed the above expression Eq. (15) in the interpretation of neutron scattering experiments.

Discussion of Im $A(K, \omega)$ and Re $D(K, \omega)$

In order to determine Im $A(K, \omega)$ or Re $D(K, \omega)$ one has to solve the dynamical problem for liquids, which is yet not possible. In the absence of the detailed knowledge of the structure of liquid one can only depend upon the phenomenological models. Several such models which describe the slow space-time variation in current or density have been formulated.

For the discussion of the quasi-elastic scattering it may be adequate to assume

$$\text{Im } A(K, \omega) = \frac{H(K)}{\pi} \frac{\Gamma(K, \omega)}{[(\omega - \omega_0)^2 + \Gamma^2(K, \omega)]}. \tag{19}$$

As a matter of fact the above expression is quite general in describing the line shape. ω_0 defines the peak position and Γ, when independent of ω, gives the width of the line and describes the damping phenomenon. $H(K)$ is given by the initial condition. For the quasielastic scattering line $\omega_0 = 0$, therefore, we can also write Eq. (19) as:

$$\text{Im } A(K, \omega) = \frac{H(K)}{2\pi} \left[\frac{1}{i\omega + \Gamma} - \frac{1}{i\omega - \Gamma} \right]. \tag{20}$$

The first term in the above expression gives the singularities of Im $A(K, \omega)$ function in the ω-plane. These may be simple poles or other kinds of singularities. We shall employ the above formalism to discuss various phenomenological models.

One may attempt to give the limiting behavior of Re $D(K, \omega)$ function.

(*i*) *Small K and small ω*

If we expand Re $D(K, \omega)$ about K and ω and take the limit, then we may replace Re $D(K, \omega)$ by the diffusion coefficient.

$$\text{Re } D(k, \omega) = D(0, 0) = D. \tag{21}$$

$$(LtK \to 0 \quad \text{and} \quad \omega \to 0)$$

In the same limit, $S(K, \omega)$ according to Eq. (14) is given by

$$S(K, \omega) = \frac{DK^2}{\pi\omega^2}. \tag{22}$$

The above result follows from the diffusion model which describes the slow space and time variation of $G_s(r, t)$ function or $S(K, \omega)$ in the small K and ω range.

(*ii*) *Small K*

If we consider the small K limit and replace Re $D(K, \omega)$ by Re $D(0, \omega)$ or $D(\omega)$ a frequency dependent function—the frequency spectrum of current or velocity correlation function then

$$S(K, \omega) = \frac{\beta\hbar K^2 D(\omega)}{\pi\omega(1 - \exp - \beta\omega\hbar)} . \tag{23}$$

One would recognize this as the one phonon expression for the harmonic vibrations in a solid. In the limit of small K this is a general result as well known in the literature.

(*iii*) *Arbitrary K and* ω

For arbitrary K and ω one must employ Eq. (13) to obtain Re $D_{\mu\nu}(K, \omega)$, which means that one must solve the dynamical problem and obtain the current density or $j(\underline{K}, t)$ its Fourier transform. In the next section, we describe several phenomenological models which have been formulated to obtain $S(K, \omega)$.

3. Phenomenological Models

We discuss various phenomenological models which have been employed in the study of the quasi-elastic scattering of neutrons in liquids.

(*i*) *Diffusion model*

As discussed by Vineyard[4] and others this model describes the slow space and time variation of the density of diffusing atoms in the hydrodynamic region. It is easy to establish that

$$\Gamma(K, \omega) = DK^2 \tag{24}$$

$$j(\underline{K}, t) = -i D\underline{K}\, \varrho(\underline{K}, t) \tag{25}$$

and

$$S(K, \omega) = \frac{DK^2}{\pi\{\omega^2 + (DK^2)^2\}} . \tag{26}$$

The pole of the response function Im $A(K, \omega)$ occurs at $i\omega = -DK^2$. This result characterizes the diffusive mode. A plot of Γ versus K^2 gives a straight line. The slope of this line gives the diffusion coefficient D.

Experimental results on the hydrogenous liquids have definitely established that the plot of Γ versus K^2 is not a straight line. The deviation from the straight line increases with the increase in K^2. As shown by the experiments of Larsson and Dahlborg[21] this deviation increases with the decrease in temperature.

The narrowing of the quasi-elastic peak with the increase in K^2 and decrease in the temperature have also opened up the possibility of studying the kinetic regime in liquids.

(*ii*) *Jump diffusion model of Singwi and Sjölander*[5]

In this model it is assumed that an atom vibrates about its mean position for a period τ_0 as in a solid and then diffuses for a period of τ_1. If we assume $\tau_0 \gg \tau_1$ then the diffusion process is instantaneous and one may consider it a jump diffusion model. For $\tau_1 \gg \tau_0$ this model reduces to the pure diffusion case discussed above.

For $\tau_0 \gg \tau_1$, the damping factor $\Gamma(K, \omega)$ and $S(K, \omega)$ for the zero phonon case are given by the following expressions.

$$\Gamma(K, \omega) = \frac{1}{\tau_0}\left\{1 - \left[\frac{\exp - 2W}{(1 + K^2 D\tau_0)}\right]\right\} \tag{27}$$

and

$$S(K, \omega) = \frac{\tau_0 \exp - 2W\left[1 - \dfrac{\exp - 2W}{(1 + K^2 D\tau_0)}\right]}{\pi\left[\omega^2\tau_0^2 + \left\{1 - \dfrac{\exp - 2W}{(1 + DK^2\tau_0)}\right\}^2\right]}. \tag{28}$$

In the above expressions D and $2W$ are the diffusion coefficient and the Debye-Waller factor respectively.

Assuming that the "neutron observation time" $\dfrac{1}{DK^2}$ is greater than the relaxation time τ_0 and also $2W$ is small we may approximate

$$\exp - 2W \approx \left(1 - K^2\overline{r^2}\right) \quad \left(\overline{r^2} \text{ is the zero point mean square displacement}\right) \tag{29}$$

$$(1 + K^2 D\tau_0)^{-1} \approx (1 - DK^2\tau_0 + D^2K^4\tau_0^2). \tag{30}$$

Therefore, from Eq. (27)

$$\Gamma(K, \omega) = DK^2\left(1 + \frac{\overline{r^2}}{D\tau_0}\right) - D^2K^4\tau_0\left(1 + \frac{\overline{r^2}}{D\tau_0}\right). \tag{31}$$

Deviation from the simple diffusion case is governed by the K^4 term, which has a coefficient involving the period of vibration τ_0.

Additional studies involving the combination of diffusive and vibratory modes have been undertaken by Oskotskii[6], Chudley and Elliot[22] and Rahman, Singwi and Sjölander.[7] The model of Rahman *et al.* has been formulated using the Langevin equation of motion for the vibratory and diffusive modes. This model involves three parameters which describe the damping of vibratory modes and the cut off frequencies for the diffusive and vibratory modes. In the case of diffusive modes the cut off frequency characterizes the delay time for the setting in of these modes. It is not possible to give $\Gamma(K, \omega)$ for this model in a simple form as the expression for $S(K, \omega)$ is quite involved due to the presence of the Langevin width function in the time integral.

(*iii*) *Single relaxation time models*

Ruijgrok[8] and Kadanoff and Martin[9] modified the diffusion model in order to take into account the short time reversible behavior and also to satisfy the moments' theorems. In this model it has been assumed that the response of the current lags behind the rapid fluctuations in the density. We write

$$\frac{\partial j(\underline{K}, t)}{\partial t} = -\frac{1}{\tau}[j(\underline{K}, t) + i\, D\underline{K}\, \varrho(\underline{K}, t)]. \tag{32}$$

τ is the relaxation time beyond which the diffusion process is important. Introducing the above result in the equation of continuity Eq. (9) we obtain

$$\left[\frac{\partial^2}{\partial t^2} + \frac{1}{\tau}\left(\frac{\partial}{\partial t} + DK^2\right)\right]\varrho(\underline{K}, t) = 0 \quad \text{for } t > 0. \tag{33}$$

It is telegrapher's wave equation which also describes the damped sound wave. Derivation of this equation from the Boltzmann equation in the case of the neutron transport problem has been given by Weinberg and Wigner.[23]

On taking the Laplace transform we obtain

$$\Gamma(K, \omega) = \frac{DK^2}{(1 + i\omega\tau)}$$

and

$$S(K, \omega) = \frac{1}{\pi}\frac{DK^2}{\left[\omega^2 + D^2\left(K^2 - \frac{\omega^2\tau}{D}\right)^2\right]}. \tag{35}$$

In this case $\Gamma(K, \omega)$ is a function of ω. However, if we assume that for small ω

$$i\omega = -DK^2 \quad \text{(Diffusion Approximation)} \tag{36}$$

then

$$\Gamma(K, \omega) = \frac{DK^2}{(1 - DK^2\tau)} \tag{37}$$

If the neutron observation time $1/DK^2$ is greater than the relaxation time τ i.e. $1 \gg DK^2\tau$ then the above expression reduces to the familiar diffusion theory result. In this approximation,

$$\Gamma(K, \omega) \approx DK^2(1 + DK^2\tau). \tag{38}$$

It is of interest to note that this model gives the deviation of Γ versus K^2 plot from the straight line in the opposite direction to the result of Singwi and Sjölander. Compare equations (31) and (38). One therefore may conclude that the relaxation times introduced in Eqs. 31 and 38 have different physical interpretations. The former describes the "energy transient" and the latter perhaps the "current transient".

(*iv*) *Egelstaff's modification*[20]

Egelstaff has proposed the following modification of Eq. (33)

$$\left(\frac{\partial^2}{\partial t^2} + J\frac{\partial}{\partial t} + L_0\right)\varrho(K, t) = 0. \tag{39}$$

J is a complex function of K and ω. From the above equation we obtain

$$\Gamma(K, \omega) = \frac{L_0}{(J + i\omega)}. \tag{40}$$

Egelstaff assumes J to be a complex function of K and ω. If we now assume that $\frac{L_0}{J} = DK^2$ and $\frac{1}{J} = \tau$ then we obtain the same expression for $\Gamma(K, \omega)$ as the single relaxation time model discussed in the previous section.

4. Extension of the Singwi-Sjölander Zero Phonon Result

The jump diffusion model of Singwi and Sjölander[5] has been extensively employed in the analysis of the quasi-elastic scattering of neutrons in hydrogenous liquids by Larsson and his group.[3] Singwi and Sjölander gave the zero phonon differential scattering cross section. We have extended this result so as to include the contribution of one phonon term

explicitly. Let us write $S(K, \omega)$ as a sum of the zero phonon (χ_0) and one phonon (χ_1) terms.

$$S(K, \omega) = \frac{1}{\pi}[\chi_0 + \chi_1]. \tag{41}$$

Using Eq. (11) of the Singwi-Sjölander paper[5] one obtains the following expressions for χ_0 and χ_1. The former has been given by Singwi and Sjölander.

$$\chi_0 = \frac{\tau_0^2 \exp - 2W b[C + \omega^2 \tau_1^2 \exp 2W]}{\tau_1 + \tau_0[b^2 + \omega^2 \tau_0^2 (f + \omega^2 \tau_1^2)]} \tag{42}$$

and

$$\chi_1 = \left(\frac{K^2}{2M}\right) \frac{\tau_0^2 \exp - 2W}{\tau_1 + \tau_0} \left[\frac{(pj + ql)\, I_0 + (pl + qj)\, I_1}{b^2 + \omega^2 \tau_0^2 (f + \omega^2 \tau_1^2)}\right] \tag{43}$$

where

$$\left.\begin{aligned}
p &= b - \omega^2 \tau_0 \tau_1 \\
q &= \omega \tau_0 \left(\alpha + \frac{\tau_1}{\tau_0}\right) \\
l &= \omega \tau_0 \left(\alpha + \frac{3\tau_1}{\tau_0}\right) \\
j &= \left(\alpha + \frac{2\tau_1}{\tau_0} + \omega^2 \tau_0 \tau_1\right) \\
b &= \alpha - \exp - 2W \\
\alpha &= 1 + K^2 D_1 \tau_1 \\
D_1 \tau_1 &= D\tau_0 \left(1 + \frac{\tau_1}{\tau_0}\right) \\
f &= \left[\frac{\tau_1^2}{\tau_0^2} + \frac{2\tau_1}{\tau_0} \exp - 2W + \alpha^2\right] \\
C &= \left[\alpha + \frac{2\tau_1}{\tau_0} + \frac{\tau_1^2}{\tau_0^2} \exp - 2W\right] \\
I_0 &= \int_{-\infty}^{+\infty} \frac{g(\xi)\, d\xi}{1 + \tau_0^2 (\omega + \xi)^2} \\
I_1 &= \int_{-\infty}^{+\infty} \frac{\tau_0 (\omega + \xi)\, g(\xi)\, d\xi}{1 + \tau_0^2 (\omega + \xi)^2} \\
g(\xi) &= \frac{f(\xi)}{\xi(\exp \xi/T - 1)}.
\end{aligned}\right\} \tag{44}$$

If we now assume that $\tau_0 \gg \tau_1$ (the jump diffusion model), then

$$\left.\begin{aligned} D_1\tau_1 &\approx D\tau_0 \\ p &= \alpha(1-\beta) \\ q &= \omega\tau_0\alpha \\ j &= \alpha \\ b &= \alpha(1-\beta); \quad C = \alpha \quad \text{and} \quad f = \alpha^2 \\ \alpha &= 1 + K^2D\tau_0 \\ \beta &= \frac{\exp - 2W}{1 + K^2D\tau_0} \end{aligned}\right\} \tag{45}$$

For χ_0 and χ_1 we obtain

$$\chi_0 = \tau_0 \exp - 2W \frac{(1-\beta)}{[\omega^2\tau_0^2 + (1-\beta)^2]} \quad \text{(Singwi-Sjölander formula)} \tag{46}$$

and

$$\chi_1 = \frac{K^2}{2M}\tau_0 \exp - 2W \frac{[\{1 - \beta + \omega^2\tau_0^2\} I_0 + \omega\tau_0(2-\beta) I_1]}{\omega^2\tau_0^2 + (1-\beta)^2}. \tag{47}$$

5. Delayed Diffusion Model

For the analysis of the quasi-elastic scattering let us discuss a delayed diffusion model. It is based upon the modification of ideas given in Vineyard's paper[4] and also in an unpublished work of Singwi. Let us divide the width function into two parts.

(a) $\gamma(t) = \gamma_{\text{diff}}(t)$ for $(t_C \leqq t \leqq \infty)$

and

(b) $\gamma(t) = \gamma_R(t)$ for $(0 < t \leqq t_C)$.

For diffusion, let us employ the following expression given by Vineyard[4]

$$\gamma_{\text{diff}}(t) = \left(- \frac{i\hbar\tau_C}{2M} + D\,|t| + D\tau_C \right) \tag{48}$$

$$\tau_C = \frac{1}{\eta} \quad \text{and} \quad D = \frac{K_BT}{M\eta} \quad \text{or} \quad \tau_C = \frac{k_BT}{MD} \quad \text{(Einstein relation)}. \tag{49}$$

The scattering law using the above width function in the time region t_C to ∞ is given by

$$S_{\text{diff}}(K, \omega) = \frac{K^2 D}{\pi[(K^2D)^2 + \omega^2]} \times \left[\cos\left(\omega t_C + \frac{\hbar\tau_C K^2}{2M}\right) - \frac{\omega}{K^2 D}\sin\left(\omega t_C + \frac{\hbar\tau_C K^2}{2M}\right)\right]. \tag{50}$$

The term outside the bracket is the Lorentzian term due to pure diffusion. Terms inside the bracket modifies this distribution. For $t_C = 0$ we get the pure diffusion result.

Therefore, one may write

$$S(K, \omega) = S_{\text{diff}}(K, \omega) + S_{\text{bound}}(K, \omega) \tag{51}$$

where

$$S_{\text{bound}}(K, \omega) = \frac{1}{2\pi}\int_{-t_C}^{t_C} \exp i\omega t \exp - K^2\gamma_R(t)\, dt. \tag{52}$$

$\gamma_R(t)$ describes the motion of the atom in the time region excluding the diffusion interval.

We shall consider two cases.

(i) Weak binding and (ii) Strong binding.

Case 1 Weak Binding

In this case we can employ the gas model $\gamma_R(t)$ with an effective temperature T_{eff},

$$\gamma_R(t) = -\frac{1}{2M}(it + i^2t^2T_{\text{eff}}) \tag{53}$$

$$\frac{T_{\text{eff}}}{T} = \int_{-\infty}^{+\infty} \cdot \left(\frac{\xi}{2T}\right)\frac{f(\xi)}{(\exp \xi/T - 1)}\, d\xi. \tag{54}$$

Therefore,

$$S_{\text{bound}}(K, \omega) = 2\sqrt{\frac{M}{K^2T_{\text{eff}}}}\int_0^{t_C^*} \cos ax \exp - x^2\, dx \tag{55}$$

where

$$t_C^* = t_C\sqrt{\frac{K^2T_{\text{eff}}}{2M}} \quad \text{and} \quad a = \left(\omega + \frac{K^2}{2M}\right)\left(\frac{2M}{K^2T_{\text{eff}}}\right)^{1/2}. \tag{56}$$

On integrating,

$$S_{\text{bound}}(K,\omega) = \sqrt{\frac{M}{4K^2T_{\text{eff}}}}\exp -\frac{a^2}{4}\left[\Phi\left(t_C^* + \frac{ia}{2}\right) + \Phi\left(t_C^* - \frac{ia}{2}\right)\right] \tag{57}$$

$$\Phi(x) = \frac{2}{\sqrt{\pi}}\int_0^x \exp - y^2\, dy = \operatorname{erf}(x). \tag{58}$$

See Grõbner and Hofreiter.[24]

For $t_C^* \to \infty$ we obtain the gas result, since $\Phi(\infty) = 1$. Employing the expansion

$$\Phi(z) = 1 - \frac{\exp - z^2}{\sqrt{\pi}\, z}\left\{1 - \frac{1}{2z^2} + \frac{1.3}{(2z^2)^2} + \frac{1.3.5}{(2z^2)^3} + \cdots\right\}. \tag{59}$$

We obtain a series expansion for $S_{\text{bound}}(K,\omega)$ which gives the correction to the standard gas formula

$$S_{\text{bound}}(K,\omega) = \sqrt{\frac{2M}{\pi K^2 T_{\text{eff}}}}\exp -\frac{1}{4}\left\{\left(\omega + \frac{K^2}{2M}\right)^2\left(\frac{2M}{K^2T_{\text{eff}}}\right)\right\} \times [1 - Q(K,\omega,\tau_C] \tag{60}$$

where the correction factor

$$Q(K,\omega,t_C) = \frac{1}{\sqrt{\pi}}\exp\left(\frac{a^2}{4} - t_C^{*2}\right) \times \left\{\frac{t_C^*\cos at_C^* + \frac{a}{2}\sin at_C^*}{\left(t_C^{*2} + \frac{a^2}{4}\right)} + \frac{1}{2}\sum_{n=1}^{\infty} F_{2n+1}\right\} \tag{61}$$

$$F_{2n+1} = (-1)^n\left\{\frac{1}{2}\cdot\frac{3}{2}\cdots\frac{2n+1}{2}\right\}\left\{\left(t_C^* - \frac{ia}{2}\right)^{2n+1}\exp - it_C^*a + \left(t_C^* + \frac{ia}{2}\right)^{2n+1}\exp it_C^*a\right\}\frac{1}{\left(t_C^{*2} + \frac{a^2}{4}\right)^{2n+1}}. \tag{62}$$

Case 2 Strong Binding

For $\gamma_R(t)$ we employ the harmonic approximation result. Undertaking the phonon expansion along the lines of Sjölander[25]

$$S_{\text{bound}}(K,\omega) = \frac{1}{2\pi}\exp -\frac{K^2}{2M}\lambda(0)\sum_{n=0}^{\infty}\left(\frac{K^2}{2M}\right)^n \times\left[\frac{1}{n!}\int_{-t_C}^{t_C}\exp i\omega t\{\lambda(t)\}^n\,dt\right] \tag{63}$$

$$\gamma_R(t) = \lambda(0) - \lambda(t) \quad \text{and} \quad \lambda(t) = \int_{-\infty}^{+\infty}\frac{f(\xi)\exp -i\xi t\,d\xi}{\xi(\exp \xi/T - 1)}. \tag{64}$$

Let us write

$$S_{\text{bound}}(K,\omega) = \sum_{n=0}^{\infty}\frac{C_n}{2\pi} \tag{65}$$

where

$$\left.\begin{aligned} C_0 &= 2\exp -\frac{K^2}{2M}\lambda(0)\,\frac{\sin\omega t_C}{\omega} \quad \text{zero phonon}\\ C_1 &= 2\left\{\exp -\frac{K^2}{2M}\lambda(0)\right\}\frac{K^2}{2M}\int_{-\infty}^{+\infty}\frac{g(\xi)\sin t_C(\omega-\xi)\,d\xi}{(\omega-\xi)} \quad \text{one phonon}\\ C_n &= \frac{\exp -\dfrac{K^2}{2M}\lambda(0)}{n!}\left(\frac{K^2}{2M}\chi(0)\right)^n G_n(\omega) \qquad n \text{ phonon.} \end{aligned}\right\} \tag{66}$$

$$\left.\begin{aligned} G_n(\omega) &= \left[\frac{1}{\lambda(0)}\right]^n\int_{-t_C}^{t_C}\left\{\prod_{i=0}^{n}\int_{-\infty}^{+\infty}g(\xi_i)\exp it(\omega-\xi_i)\right\}dt\\ g(\xi) &= \frac{f(\xi)}{\xi(\exp \xi/T - 1)}. \end{aligned}\right\} \tag{67}$$

For $n \geqq 2$ one may employ the central limit theorem. Rewriting

$$G_n(\omega) = \frac{1}{2}\int_{-t_C}^{t_C}\exp i\omega t\exp\left\{n\ln\frac{\lambda(t)}{\lambda(0)}\right\}dt. \tag{68}$$

We also approximate

$$n \ln \frac{\lambda(t)}{\lambda(0)} \simeq n \left\{ \frac{it}{\lambda(0)} + \frac{i^2 t^2}{2} \Delta^2 + \cdots \right\} \tag{69}$$

$$\Delta^2 = \left[\frac{\langle \xi \rangle}{\lambda(0)} - \frac{1}{\lambda(0)^2} \right]. \tag{70}$$

Therefore,

$$G_n(\omega) = \sqrt{\frac{2}{\Delta^2}} \int_{-\frac{\Delta t_C}{\sqrt{2}}}^{\frac{\Delta t_C}{\sqrt{2}}} \exp i\, za \exp - z^2\, dz \tag{71}$$

with

$$a = \left(\omega + \frac{n}{\lambda(0)} \right) \sqrt{\frac{2}{\Delta^2}} \tag{72}$$

$$z^2 = \frac{t^2 \Delta^2}{2}. \tag{73}$$

As shown for the weak binding case,

$$G_n(\omega) = \sqrt{\frac{\pi}{2\Delta^2}} \exp - \frac{a^2}{4} \left[\Phi\left(\frac{\Delta t_C}{\sqrt{2}} - \frac{ia}{2} \right) + \Phi\left(\frac{\Delta t_C}{\sqrt{2}} + \frac{ia}{2} \right) \right] \tag{74}$$

For $t_C \to \infty$ we obtain the result given in the Sjölander's paper.

It must, however, be pointed out that at $t = t_C$ where the vibratory mode undergoes an abrupt transformation into the diffusive mode is physically not convincing. One may, therefore, have to develop a different model to describe the intermediate time region between the vibratory and diffusive modes. But then it is the crux of the problem.

In a recent study Ardente *et al.*[26] decomposed the width function $\gamma(t)$ into two parts:

(i) $\gamma_I(t)$ corresponding to a damped harmonic oscillator discussed by Chandrasekhar[27] and Wang and Uhlenbeck.[28]

(ii) $\gamma_{II}(t)$ corresponding to the Langevin diffusion model. See Vineyard.[4]

Undertaking the Fourier transform and the standard phonon expansion (involving the Bessel functions along the lines of Zemach and Glauber[29], these authors have given an expression for $S(K, \omega)$ in a series

form involving two relaxation times τ_I and τ_{II}. The former describes the damping of harmonic modes and is given by the interatomic potential and the latter by the Einstein's relation in terms of the diffusion constant of the medium.

In contrast to the delayed diffusion model presented in this study Ardente *et al.*[26] assume the existence of diffusive and harmonic modes at all times.

A discussion of various phenomenological models considered in section 3 has also been given by Sjölander[30] in his recent review article.

6. "Microscopic Diffusion Cooling"

Two experimental facts emerge out from the cold neutron scattering experiments.

1. Narrowing of the quasi-elastic line, that is the deviation of the plot of Γ (half width of the quasi-elastic line) versus K^2 from a straight line.

2. Temperature dependence of this deviation. Experiments of Larsson and Dahlborg[21] on the hydrogenous liquids have definitely established that this deviation increases with the decrease in temperature.

In the light of above experimental observations one is tempted to speculate a "microscopic diffusion cooling" phenomenon arising due to the overlap of the kinetic and hydrodynamic regimes in fluids.

It is of interest to note that one encounters similar facts in the description of the macroscopic diffusion cooling phenomenon in the transport of neutrons in solids and liquids. Von Dardel and Sjostrand[31] have discussed this effect in describing the decay of a pulse of neutrons in a finite moderating medium. Biondi[32] and Parker[33] have considered the diffusion cooling effect in the discussion of the transport of electrons in a gas. The macroscopic diffusion cooling phenomenon is a consequence of mixing between thermalization and diffusion processes. Let us describe the macroscopic diffusion cooling.

The asymptotic decay of a pulse of neutrons in a finite nonabsorbing medium (larger in size than the transport mean free path) is given by

$$\lambda = DB^2 - CB^4. \tag{75}$$

In the above equation λ is decay constant, D is the diffusion coefficient of transport of neutrons, B is the geometrical buckling which defines the

size of the system and C is the diffusion cooling coefficient. The latter parameter is a measure of the mixing between neutron thermalization and diffusion processes. In the case of pure diffusion of neutrons $\lambda = DB^2$. One may also define λ and B as the Laplace and Fourier transform variables of time and space respectively in the linearised Boltzmann equation which describes the transport of neutrons.

C may be expressed in terms of the relaxation time τ, for the establishment of the Maxwellian velocity distribution of neutrons in a non-absorbing and infinite medium, following Nelkin[34] and Purohit.[35]

$$C = \frac{2\tau D^2}{3\pi}. \tag{76}$$

The relaxation time τ increases with the increase in the degree of binding of atoms in the system. Therefore, τ and C will increase with the decrease in temperature.

Let us now write Γ, the half width of the quasi-elastic line in terms of K^2 in the following form

$$\Gamma = DK^2 - CK^4. \tag{77}$$

Γ and K are the Laplace and Fourier transform variables of time and space respectively in the microscopic transport equation. On the other hand, λ and B are the similar transform variables in the macroscopic transport equation. Equations (77) and (75) describe the deviation from diffusion process on microscopic and macroscopic time scales.

For the sake of further discussion if we compare Eqs. (31) and (77) we obtain an expression for C

$$C = \tau_0 D^2. \tag{78}$$

The similarity of two expressions for C in macroscopic and microscopic cases described by Eqs. (76) and (78) is very striking. It is of interest to note that Eq. (75) or (77) would qualitatively describe the narrowing effect and its temperature dependence.

In order to demonstrate the existence of the "microscopic diffusion cooling" phenomenon conclusively one will have to calculate

$$\langle v(K^2, t = \infty)\rangle = \underset{\substack{-\infty \\ Lt\, t\to\infty}}{\overset{+\infty}{\int}} \int_0 VF(r, v, t) \exp(-i\underline{K} \cdot \underline{r})\, dv\, d\underline{r} \tag{79}$$

and demonstrate that

$$\langle v(K^2, t = \infty)\rangle = \langle v(K^2 = 0, t = \infty)\rangle \{1 - CK^2 + \cdots\}. \tag{80}$$

7. Conclusion

In this study we have presented a discussion of various phenomenological models in the frame work of general formalism involving a generalized damping factor $\Gamma(K, \omega)$. It has been emphasized that this factor governs the width of the quasi-electric scattering line as a function of K^2. We have also pointed out that the relaxation times introduced by different authors may not have the same physical meaning. For example, the relaxation time introduced by Kadanoff and Martin[9] may refer to the collisions of "lossful" nature. On the other hand, the relaxation times of Nelkin and Ghatak[10] and of Gibbs and Ferziger[11] correspond to collisions of "loss less" nature. For a discussion of collisions of "lossful" and "loss less" nature, see Chester.[36]

In addition to the discussion of various phenomenological models, we have derived $S(K, \omega)$ for a delayed diffusion model and have also extended the zero phonon result for $S(K, \omega)$ of the Singwi-Sjolander model[5], so as to include one phonon contribution.

Alternative to the use of these models is to numerically generate $G(r, t)$ function as pioneered by Rahman[37] for the Lennard-Jones potential for the liquid Argon and extended by Paskin and Rahman[38] for the long range oscillatory potential for the liquid metal Na. The discussion of these numerical results in terms of the dynamical modes in fluids and the construction of $S(K, \omega)$ from calculated $G(r, t)$, to analyze the neutron scattering data constitute important areas of investigation.

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