ELASTIC SCATTERING OF NEUTRONS AND THE MÖSSBAUER EFFECT IN SYSTEMS WITH LOCAL DEGREES OF FREEDOM

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Some possibilities are discussed for investigating the lifetime and the law of motion relative to local degrees of freedom of atomic systems by means of experiments on quasielastic incoherent scattering of slow neutrons and by the Mössbauer effect. In particular, it is shown that under conditions of "poor resolution" the dependence of the probabilities for these effects on momentum transfer and temperature of the medium differs essentially from that for a system without local states. For example, for large momenta one may even observe an increase of the probability with temperature.

1. It is well known that inelastic (incoherent) scattering of slow neutrons in matter is an effective method for studying the energy spectrum of atomic motions and in particular for determining the energy levels of motion relative to local degrees of freedom such as, for example, hindered rotation in water.[1] Analysis of peak shapes in the energy distribution of inelastically scattered neutrons for which such degrees of freedom are excited enables one to obtain additional information about the nature of the local motion. Thus, from the peak width one can evaluate the lifetime of the quanta of the local state; but such an estimate, strictly speaking, gives only an upper limit for the lifetime, since a broadening of the spectrum may also be caused by the spread of the energy level due to inhomogeneity of the system.

The present paper shows that from an analysis of elastic (more precisely, quasielastic) scattering of neutrons one can obtain additional valuable information about the energy levels corresponding to local degrees of freedom and, in particular, about their lifetime. Similar information can also be gotten from a study of the Mössbauer effect.

2. The expression for the differential cross section for incoherent scattering of slow neutrons by some (definite[1]) nucleus in an atomic system can be written in the form[2]

$$\frac{\partial^2\sigma}{\partial\Omega\,\partial E}=\frac{a^2}{2\pi\hbar}\,\frac{p}{p_0}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}S(\varkappa,\ t),$$

$$S(\varkappa,\ t)=\langle e^{i\varkappa\hat{\mathbf{R}}(0)}e^{-i\varkappa\hat{\mathbf{R}}(t)}\rangle. \qquad (1)$$

Here a is the incoherent scattering length from an infinitely heavy nucleus; $\mathbf{p}_0$ and $\mathbf{p}$ are the initial and final neutron momentum; $\hbar\boldsymbol{\varkappa}=\mathbf{p}_0-\mathbf{p}$, $\hbar\omega=(p_0^2-p^2)/2m$ (where m is the neutron mass); $\hat{\mathbf{R}}(t)$ is the Heisenberg operator for the coordinate of the scattering nucleus. The symbol $\langle\ldots\rangle=\Sigma_i g_i\langle i|\ldots|i\rangle$ denotes a quantum mechanical and statistical average over the states $|i\rangle$ (g_i is the probability that the system is initially in state $|i\rangle$).

The elastic scattering cross section is given by (1) with the correlation function $S(\varkappa,t)$ replaced by its asymptotic expression for $t\to\infty$. For atomic systems which have no local degrees of freedom, the function $S(\varkappa,t)$ practically reaches its asymptotic form after a small number of mean periods of atomic motion, T_D. If, however, the system has local degrees of freedom (say one, for simplicity), then at large times[2]

$$S(\varkappa,\ t)=S_0(\varkappa,\ \infty)+e^{-|t|/\tau}S_1(\varkappa,\ \infty),$$

$$S_0(\varkappa,\ \infty)=|\langle e^{i\varkappa\mathbf{R}}\rangle|^2,$$

$$S_1(\varkappa,\ \infty)=\sum_i g_i|\langle i|e^{i\varkappa\mathbf{R}}|i\rangle|^2-S_0(\varkappa,\ \infty), \qquad (2)$$

where τ is the lifetime for the excitation of the local degree of freedom, and $\tau\gg T_D$, so that the approach of $S(\varkappa,t)$ to its asymptotic form occurs much more slowly. As the local degree of freedom becomes more and more collectivized, $S_1(\varkappa,t)$

[1] We shall omit the index labeling the particular nucleus.

[2] In those cases where $S(\varkappa,t)$ has no limit for $t\to\infty$, as, for example, for the oscillator, we mean the average of $S(\varkappa,t)$ over a time interval much greater than T_D.[3]

approaches zero. In the case of a light impurity in a heavy lattice with anharmonic binding, an expression of the form of (2) was obtained and analyzed by Krivoglaz and Visscher.[4]

Thus the cross section for quasielastic scattering of neutrons should depend significantly on whether local degrees of freedom are or are not present.

3. Suppose that the apparatus resolution is a gaussian of width Δ. Then the experimentally measured cross section for quasielastic scattering is actually the quantity

$$\left(\frac{d\sigma}{d\Omega}\right)^{\text{el}}_{\text{exp}} \sim \int_{-\infty}^{\infty} dt\, e^{-\Delta^2 t^2} [S_0(\varkappa, \infty) + e^{-|t|/\tau} S_1(\varkappa, \infty)]$$

$$= \frac{\sqrt{\pi}}{\Delta} S_0(\varkappa, \infty) + \frac{2S_1(\varkappa, \infty)}{\Delta} \int_0^{\infty} dx\, e^{-x^2 - x/\Delta\tau}. \quad (3)$$

In particular for $\tau\Delta \gg 1$ (poor resolution)

$$\left(\frac{d\sigma}{d\Omega}\right)^{\text{el}}_{\text{exp}} \sim \frac{\sqrt{\pi}}{\Delta} [S_0(\varkappa, \infty) + S_1(\varkappa, \infty)], \quad (4)$$

for $\tau\Delta \ll 1$ (good resolution)

$$\left(\frac{d\sigma}{d\Omega}\right)^{\text{el}}_{\text{exp}} \sim \frac{\sqrt{\pi}}{\Delta} S_0(\varkappa, \infty). \quad (5)$$

Thus by studying the quasielastic incoherent scattering of slow neutrons with different resolutions (or by measuring the shape of the quasielastic peak in the case of good resolution), one can determine the lifetime of the excitation of the local degree of freedom. If we take $\tau \sim 10^{-11}$—10^{-12} sec (for crystals at relatively high temperature or for liquids), such experiments require a resolution of $\hbar\Delta \sim 10^{-5}$—10^{-4} eV, which can already be achieved with present day equipment.

A similar situation also exists for the Mössbauer effect. The cross section for recoilless absorption of a γ quantum (with momentum p) is

$$\sigma(\mathbf{p}) = \frac{\sigma_0 \Gamma}{4\hbar} \int_{-\infty}^{\infty} dt \exp\left(-\frac{\Gamma|t|}{2\hbar} - it\frac{pc - E_0}{\hbar}\right) \lim_{t\to\infty} S(\mathbf{p}, t), \quad (6)$$

where σ_0 is the resonance absorption cross section, and E_0 and Γ are the position and width of the resonance level. Substituting (2) in (6), we get

$$\sigma(\mathbf{p}) = \frac{\sigma_0 \Gamma^2}{4} \left\{ \frac{S_0(\mathbf{p}, \infty)}{\Gamma^2/4 + (pc - E_0)^2} + \frac{(1 + \hbar/\tau\Gamma) S_1(\mathbf{p}, \infty)}{\Gamma^2/4 (1 + \hbar/\tau\Gamma)^2 + (pc - E_0)^2} \right\}, \quad (7)$$

i.e., the cross section is a superposition of two Lorentz shapes with different widths. Since W is the probability for the Mössbauer effect (for a thin sample), and is thus quadratic in $\sigma(p)$, for the case where $\Gamma\tau/\hbar \gg 1$ ("poor resolution"),

$$W \sim [S_0(\mathbf{p}, \infty) + S_1(\mathbf{p}, \infty)]^2, \quad (8)$$

while for $\Gamma\tau/\hbar \ll 1$ ("good resolution")

$$W \sim [S_0(\mathbf{p}, \infty)]^2. \quad (9)$$

Therefore by making experiments with short-lived and longlived Mössbauer isotopes embedded as impurities in a lattice, one can also determine the lifetime of the local excitation. The Mössbauer effect has been observed in isotopes for which $\hbar/\Gamma$ is in the range from 10^{-7} sec (Fe^{57}) to 10^{-11} sec (Re^{187}, E_γ = 134 keV).

Thus the ranges in which one can do experiments on elastic incoherent scattering and on the Mössbauer effect practically overlap.

4. Now let us estimate the expected effect. For harmonic oscillations, with frequency ω_0 and polarization vector e,[3] of an atom with mass M at temperature T,

$$S_0(\varkappa, \infty) + S_1(\varkappa, \infty) = F_{\text{harm}}\left(\frac{\hbar\omega_0}{2kT}, \frac{\varkappa e}{\sqrt{2\hbar\omega_0 M}}\right), \quad (10)$$

$$F_{\text{harm}}(\beta, y) = \exp[-y^2 \operatorname{cth}\beta]\, I_0\left(\frac{y^2}{\operatorname{sh}\beta}\right);$$

$$S_0(\varkappa, \infty) = F'_{\text{harm}}\left(\frac{\hbar\omega_0}{2kT}, \frac{\varkappa e}{\sqrt{2\hbar\omega_0 M}}\right),$$

$$F'_{\text{harm}}(\beta, y) = \exp[-y^2 \operatorname{cth}\beta]. \quad (10')*$$

Thus in the case of neutron scattering the effect is

$$\frac{S_1(\varkappa, \infty)}{S_0(\varkappa, \infty)} = I_0\left(\frac{(\varkappa e)^2}{2\hbar\omega_0 M} \frac{1}{\operatorname{sh}(\hbar\omega_0/2kT)}\right) - 1 \quad (11)$$

and, in particular, for the torsional oscillations in water[1] (M_{eff} = 2.32 m, $\hbar\omega_0$ = 0.06 eV, kT = 0.025 eV, $\hbar^2\kappa^2/2m$ = 0.18 eV, i.e., $S_0(\kappa, \infty) = 0.2$), we get $S_1(\kappa, \infty)/S_0(\kappa, \infty) = 0.2$, i.e., a quite sizable value.

In the case of the Mössbauer method, for the classical Mössbauer nucleus Ir^{191} (E_γ = 129 keV, lifetime 10^{-10} sec), with $\hbar\omega_0$ = 0.024 eV and kT = 0.008 eV, i.e., for $S_0(\kappa, \infty) = 0.11$, we have

$$(S_1(\varkappa, \infty)/S_0(\varkappa, \infty) + 1)^2 - 1 = 0.5.$$

Similar results are found for other laws of motion relative to the local degree of freedom, such as strongly anharmonic vibrations, rotation, etc. It should be noted that one can treat in similar fashion atomic systems with collectivized degrees of freedom for which the spectral density is localized in a narrow frequency range $\delta\omega$, small

[3] The value of e^2 determines the contribution of the local vibration to the total motion of the given atom. For vibration of a light impurity atom in a heavy lattice, $e^2 \sim 1$. The deviation of e^2 from unity can be taken into account by introducing an effective mass M_{eff}.

*sh = sinh, cth = coth.

compared to the average frequency $\bar{\omega}$ of collective motion. Then if the apparatus resolution is poor ($\Delta > \delta\omega$), such a collective motion has the same effect on the experiment as a local mode. Examples of such "quasilocal" motions are the optical vibrations of a crystal lattice containing markedly different masses in a unit cell, and the vibration of a heavy impurity atom in a light host, for which it is known[6] that one can have the condition $\delta\omega \ll \bar{\omega}$.

5. Now let us consider other possible ways of detecting and studying local motion of atoms. From here on we shall be talking about quasielastic neutron scattering and the Mössbauer effect under conditions of "poor resolution" (probability proportional to $S(\kappa) = S_0(\kappa, \infty) + S_1(\kappa, \infty)$), since the locality can manifest itself only under such conditions.

It follows directly from formulas (10) and (10′) that the temperature dependence of the function $S(\kappa)$ is essentially different for local and collective degrees of freedom. Thus the contribution to the total function $S(\kappa)$ from a local vibration (formula 10) decreases much more slowly with increasing temperature T than the contribution from a collective vibration (formula 10′), while under certain conditions (when $(\kappa \cdot e)^2/2M\hbar\omega_0 > 2$) in the low temperature region it even increases initially with increasing T. This peculiar behavior of $S(\kappa)$ is illustrated in Fig. 1, which shows the dependence of $F_{harm.}(\beta, y)$ on β for a few values of y^2; the curves for $y^2 > 2$ have a definite maximum.

The occurrence of this maximum is not a special property for harmonic vibrations. To see this we consider the function $S(\kappa)$ for an arbitrary system in the limit of low temperatures.

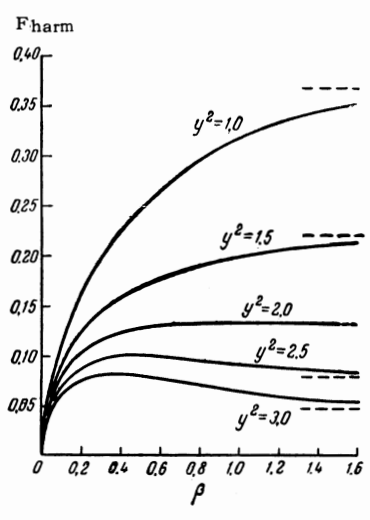

FIG. 1

Considering that under conditions of poor resolution $S(\kappa)$ for one degree of freedom (q, e) is given by the general formula

$$S(\varkappa) = \sum_i g_i |\langle i | \exp(i\varkappa e q/\hbar) | i\rangle|^2,$$

$$g_i = \Big[\sum_j \exp(-E_j/kT)\Big]^{-1} \exp(-E_i/kT) \qquad (12)$$

(where g_i is the probability that the motion relative to the coordinate q is described by the wave function $|i\rangle$ with energy E_i), we obtain, for $T \to 0$,

$$S(\varkappa) = |\langle 0|\exp(i\varkappa e q/\hbar)|0\rangle|^2 + \exp(-(E_1 - E_0)/kT)\, s, \qquad (13)$$

$$s = |\langle 1|\exp(i\varkappa e q/\hbar)|1\rangle|^2 - |\langle 0|\exp(i\varkappa e q/\hbar)|0\rangle|^2. \qquad (14)$$

From this we see that S decreases with temperature ($s < 0$) if the probability for "elastic" interaction in the first excited state is less than in the ground state, while S increases if the probability for elastic interaction in the first excited state is greater than in the ground state.

Consider s as a function of κ. For low momentum transfers

$$s \propto D_0 - D_1, \qquad D_i = \langle i|q^2|i\rangle - |\langle i|q|i\rangle|^2. \qquad (15)$$

Since the dispersion of the displacements D_i as a rule increases with increasing excitation (for example, for the oscillator $D_1 = 3D_0$), in the limit of low momenta $s < 0$, and consequently S decreases with temperature. But systems are possible for which $D_1 \lesssim D_0$ (for example, for the rigid rotator, treated later in Sec. 6), and then this statement is incorrect. With increasing κ, the quantity $|\langle 1|\exp(i\kappa \cdot eq/\hbar)|1\rangle^2$ usually decreases more slowly than does $|\langle 0|\exp(i\kappa \cdot eq/\hbar)|0\rangle^2$, since the first quantity is the Fourier component of a more rapidly oscillating function. Thus as κ increases the quantity s may change sign, i.e., starting from some value for the momentum transfer, S will increase with temperature (for example, for the oscillator when $(\kappa \cdot e)^2/2M\hbar\omega_0 > 2$). The corresponding value is $\kappa_{crit.} \sim \hbar/R_0$, where R_0 is the effective size of the region within which the probability density is significantly different from zero.

We should emphasize that these arguments are not absolute; it is possible to have systems for which s is always less than zero (for example, motion in an attractive Coulomb field). Strictly speaking, an increase of $S(\kappa)$ with temperature will be observed for systems where the effective size R_0 in the first excited state is not markedly greater than the value of R_0 in the ground state.

6. Let us consider some examples.

A. The rigid rotator.

$$S(\varkappa) = F_{r.r}\ (\hbar^2/2JkT,\ pR_0/\hbar),$$

$$F_{r.r}\ (\beta, y) = \Big[\sum_{l=0}^{\infty} (2l+1)\, e^{-l(l+1)\beta}\Big]^{-1}$$

$$\times \sum_{l=0}^{\infty}\sum_{L=0}^{\infty} (2l+1)^2 e^{-l(l+1)\beta} j_L^{\,2}(y)\,(L0\,|\,l0l0)^2, \qquad (16)$$

where R_0 is the distance of the nucleus from the center of inertia of the rotator, J is its moment of inertia, while $j_L(x)$ is a spherical Bessel function. For low temperatures ($\beta \to \infty$)

$$F_{r.r}\ (\beta, y) = j_0^2(y) + 6e^{-2\beta} j_2^2(y),$$

i.e., it increases with temperature for all values of the momentum.

The expression (16) simplifies in the limiting cases of large and small momenta:

$$F_{r.r}\ (\beta, y) = j_0^2(y) + j_2^2(y)\, A(\beta), \quad y \to 0,$$

$$A(\beta) = 5\Big[\sum_{l=0}^{\infty} (2l+1)\, e^{-l(l+1)\beta}\Big]^{-1} \sum_{l=0}^{\infty} \frac{l(l+1)(2l+1)}{(2l-1)(2l+3)}\, e^{-l(l+1)\beta};$$

$$F_{r.r}\ (\beta, y) = y^{-2}\sin^2 y B(\beta), \quad y \gg 1,$$

$$B(\beta) = \Big[\sum_{l=0}^{\infty} (2l+1)\, e^{-l(l+1)\beta}\Big]^{-1} \sum_{l=0}^{\infty} (2l+1)^2\, e^{-l(l+1)\beta}.$$

Graphs of the dependence of the functions A and B on β are given in Fig. 2 (the dashed curves are the asymptotic forms of A and B: $A(\beta) = 5/4$, $B(\beta) = (\pi/\beta)^{1/2}$ for $\beta \to 0$; $A(\beta) = 6e^{-\beta}$, $B(\beta) = 1 + 6e^{-2\beta}$ for $\beta \to \infty$). We see that $F_{r.r.}(\beta, y)$ increases with temperature up to large values of T ($\beta \lesssim 0.1$).

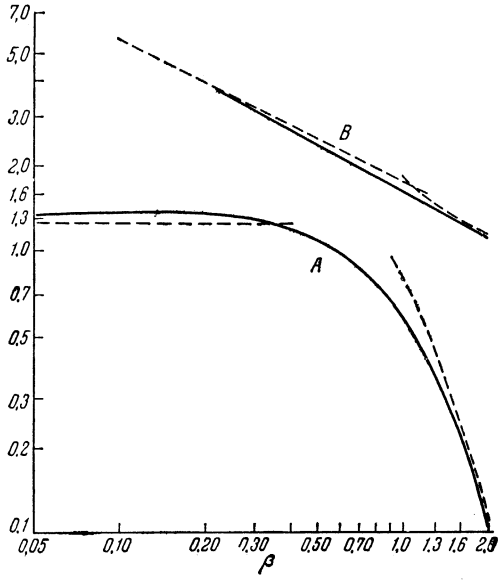

FIG. 2

B. Square potential well with infinitely steep sides (width a).

$$S(\varkappa) = F_{anharm}(\beta, y)$$

$$= \frac{\sin^2 \pi y}{\pi^2 y^2}\, \Phi_0^{-1}(\beta) \sum_{n=1}^{\infty} e^{-\beta n^2} \left(\frac{n^2}{y^2 - n^2}\right)^2, \qquad (17)$$

$$\Phi_m(\beta) = \sum_{n=1}^{\infty} \frac{1}{n^m}\, e^{-\beta n^2}, \qquad y = \frac{\varkappa e}{2\pi\hbar}\, a, \qquad \beta = \frac{\pi^2\hbar^2}{2MkTa^2}.$$

In particular, for low momentum transfers ($y \ll 1$)

$$F_{anharm}(\beta, y) = 1 - y^2\left[\frac{\pi^2}{3} - 2\frac{\Phi_2(\beta)}{\Phi_0(\beta)}\right],$$

i.e., it decreases with increasing T, while for large $y \gg 1$, and under the condition $\beta y^2 \gg 1$,

$$F_{anharm}(\beta, y) = \frac{3}{4}\frac{\sin^2 \pi y}{\pi^2 y^2 \beta^2}, \qquad (18)$$

i.e., it increases with temperature. As is easily verified, in the low temperature region ($\beta \to \infty$) the quantity $F_{anharm.}$ increases with temperature for $y > \sqrt{8/5}$, and decreases when $y < \sqrt{8/5}$. Figure 3 shows the function $F_{anharm}(\beta, y)$ in its dependence on β for a few values of y. As expected, for sufficiently large momenta ($y \gtrsim 1.5$) one finds a temperature maximum. With increasing y this maximum shifts toward higher temperatures. Formula (18) is very instructive in this respect, indicating that for large y the quantity $S_{anharm.}$ increases like T^2 over a wide range of temperatures.

It is possible that the peculiar temperature dependence of the Mössbauer effect on krypton embedded in organic compounds [7] can be explained by this effect. Unfortunately the lack of detailed data prevents a more thorough analysis.

7. In practice the observation of the peculiarities in the temperature behavior of $S(\kappa)$, when local degrees of freedom are present, is made

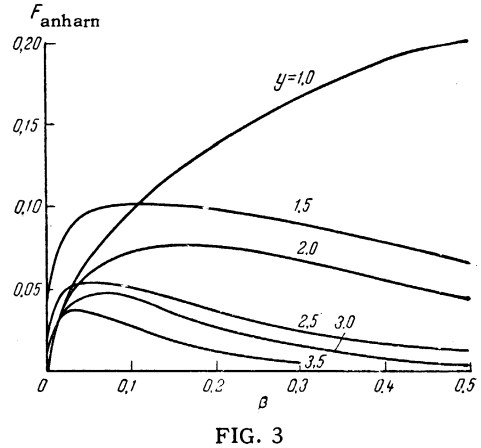

FIG. 3

difficult by the necessity for separating this effect from the background produced by the large number of collective degrees of freedom. This difficulty can be overcome by observing the dependence of the probability on the square of the momentum transfer, since the collective degrees of freedom give a contribution to this probability which is proportional to $\exp(-\text{const}\cdot\kappa^2)$, and the whole of the deviation from such a dependence is associated with local degrees of freedom.

In the case of quasielastic scattering of neutrons there is the additional difficulty that one must separate the quasielastic incoherent scattering.

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