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Resonance Absorption of Nuclear Gamma Rays and the Dynamics of Atomic Motions*

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The theory of resonance absorption of nuclear γ rays is generalized for an arbitrary system of interacting particles by expressing the relevant transition probability in terms of a space-time self-correlation function; and thus relating the resonance line shape to the incoherent differential scattering cross section for slow neutrons. Two limiting cases: (i) a gas and (ii) a solid have been considered. Discussion regarding the justification of the use of a classical self-diffusion function for a liquid is given and expressions for the broadening of the resonance line due to diffusive motions of the atoms of the interacting system are derived. It is suggested how Mössbauer-type experiment could be used to give information regarding the diffusive motions of atoms in a solid and also, under more favorable circumstances, in a liquid.

INTRODUCTION

THE observation by Mössbauer[1] that nuclear γ rays can be resonantly absorbed or scattered by nuclei bound in a crystal lattice has recently led to some very interesting applications[2] and holds promise for more applications particularly in the field of solid-state physics. Mössbauer's observation rests on the fact that in the case of a nucleus bound in a crystal, a γ ray can be emitted or absorbed without any energy transfer to and from the lattice. The probability of such a recoilless transition is, in most cases, small and is governed by the usual Debye-Waller factor, familiar in the theory of x ray and neutron scattering. Mössbauer explained his experimental results on the basis of a theory due to Lamb[3] for the Doppler broadening of neutron absorption resonance. Both in the theory of neutron and γ-ray resonance absorption the relevant matrix element corresponding to a transition of the crystal lattice from one state to the other is the same.

The purpose of this paper is two-fold: one is to generalize the theory for an arbitrary system of interacting particles by expressing the transition probability in terms of a space-time self-correlation function, which as is well known, determines the incoherent scattering for slow neutrons; and the second is to show how Mössbauer technique can be used to gain information concerning the nature of diffusive motions of atoms in a solid and also, under more favorable circumstances, in a liquid. The cross section for γ-ray resonance absorption in the case of a gas (Bethe Placzek formula in the case of neutrons) and in the case of a solid, in the limit of both weak and strong binding (two limiting cases of Lamb's theory in the case of neutrons), follows very simply from one general formula. Furthermore, the generalized formula can be of great help in more complicated systems as for instance liquids, where it is difficult to treat the dynamics of atomic motions in detail.

MATHEMATICAL FORMULATION

We are interested in calculating the probability of absorption or emission of a γ ray of momentum $\mathbf{p}$ by a single nucleus of an interacting system (say solid or liquid) such that the nucleus makes a transition from a state A to a state B and at the same time the interacting system makes a transition from a state, say $|n0\rangle$ to a state $|n\rangle$. Since the interaction within a nucleus is much stronger than that between two nuclei, the total wave function can be written as a product of wave functions one of which depends only on the coordinates of the centers of masses of different nuclei and the other depends on the coordinates of the nucleons relative to the centers of masses of their respective nuclei. The transition matrix element, corresponding to the absorption of a photon, can be written as $\langle Bn|H'|n0Ap\rangle$, where H' represents the interaction between the radiation field and the nucleus and has the following form:

$$H'=\sum_i ca_{\mathbf{p}} \exp(i\mathbf{p}\cdot\mathbf{r}_i/\hbar) =\exp(i\mathbf{p}\cdot\mathbf{R}_a/\hbar) \sum_i ca_{\mathbf{p}} \exp[i\mathbf{p}\cdot(\mathbf{r}_i-\mathbf{R}_a)/\hbar].$$

c is a constant depending on $\mathbf{p}$, $a_{\mathbf{p}}$ is the annihilation operator for a photon with momentum $\mathbf{p}$, $\mathbf{r}_i$ is the coordinate of a nucleon of the nucleus a, and $\mathbf{R}_a$ is the coordinate of the center of mass of the nucleus. The interaction operator H' is thus a product of two terms, one of which depends only on the coordinates of the nucleons relative to their center of mass and the other depends only on the coordinates of the center of mass. Thus the matrix element of the transition is a product of two matrix elements, one of which corresponds to the change in the internal state of the nucleus and the other is $\langle n|\exp(i\mathbf{p}\cdot\mathbf{R}_a/\hbar)|n0\rangle$, corresponding to a change in the state of the collective motions of the centers of masses. The first matrix element is just a constant for our purpose, and it is the second one with which we shall be mainly concerned here. It then follows

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[1] R. L. Mössbauer, Z. Physik **151**, 124 (1958); Naturwissenschaften **45**, 538 (1958); Z. Naturforsch **14a**, 211 (1959).

[2] During the last year and this year a number of communications concerning the Mössbauer effect and its various applications have appeared in the Physical Review Letters to which the reader is referred.

[3] W. E. Lamb, Phys. Rev. **55**, 190 (1939).

from the usual dispersion theory[4] that the absorption cross section per nucleus for a γ ray of energy E is given by

$$\sigma_a(E)=\frac{\sigma_0\Gamma^2}{4}\sum_{n,n0} g_{n0}\frac{|\langle n|\exp(i\mathbf{p}\cdot\mathbf{R}/\hbar)|n0\rangle|^2}{(E_0-E+\epsilon_n-\epsilon_{n0})^2+\Gamma^2/4}, \tag{1}$$

where E_0 is the energy difference between the final and the initial nuclear states of the absorbing nucleus, ϵ_n and ϵ_{n0} are, respectively, the energies of the states $|n\rangle$ and $|n0\rangle$ of the interacting system, Γ is the natural width of the excited state of the nucleus and g_{n0} is the statistical weight factor for the state $|n0\rangle$. In Eq. (1) the nuclear width Γ has been assumed to be independent of the state $|n\rangle$. Also the suffix a in $\mathbf{R}$ has been omitted. The constant before the summation sign has been so chosen that $\sigma_a(E)$ goes over to the familiar Breit-Wigner formula for a fixed nucleus, σ_0 being the resonance absorption cross section.

Now Eq. (1) can be written as follows:

$$\begin{aligned}\sigma_a(E)&=\frac{\sigma_0\Gamma^2}{4}\sum_{n,n0} g_{n0}|\langle n|\exp(i\mathbf{p}\cdot\mathbf{R}/\hbar)|n0\rangle|^2\int_{-\infty}^{\infty}\frac{\delta[\rho-(\epsilon_n-\epsilon_{n0})/\hbar]}{(E-E_0-\hbar\rho)^2+\Gamma^2/4}d\rho\\
&=\frac{\sigma_0\Gamma^2}{4}\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\{\sum_{n,n0} g_{n0}|\langle n|\exp(i\mathbf{p}\cdot\mathbf{R}/\hbar)|n0\rangle|^2\exp[it(\epsilon_n-\epsilon_{n0})/\hbar]\}\\
&\quad\times\int_{-\infty}^{\infty}\frac{\exp(-it\rho)}{(E-E_0-\hbar\rho)^2+\Gamma^2/4}d\rho\\
&=\frac{\sigma_0\Gamma}{4\hbar}\int_{-\infty}^{\infty}\exp[-it(E-E_0)/\hbar-(\Gamma/2\hbar)|t|]dt\\
&\quad\times[\sum_{n,n0} g_{n0}\langle n0|\exp(-i\mathbf{p}\cdot\mathbf{R}/\hbar+itH/\hbar)|n\rangle\langle n|\exp(i\mathbf{p}\cdot\mathbf{R}/\hbar-itH/\hbar)|n0\rangle]\\
&=\frac{\sigma_0\Gamma}{4\hbar}\int_{-\infty}^{\infty}\exp[-it(E-E_0)/\hbar-\Gamma/2\hbar|t|]\langle\exp[-i\mathbf{p}\cdot\mathbf{R}(0)/\hbar]\exp[i\mathbf{p}\cdot\mathbf{R}(t)/\hbar]\rangle_T dt,\end{aligned} \tag{2}$$

where $\mathbf{R}(t)$ is the Heisenberg operator defined by

$$\mathbf{R}(t)=\exp(itH/\hbar)\mathbf{R}\exp(-itH/\hbar).$$

H being the Hamiltonian of the interacting system, and $\langle\cdots\rangle_T$ means both the quantum mechanical and the statistical average at temperature T. We shall here restrict ourselves to a system for which Boltzmann statistics is applicable. In the above derivation the Fourier representation of the δ function and the identity $\sum_n|n\rangle\langle n|=1$ have been used. We now define a function $G_s(\mathbf{r},t)$ through the following equation

$$\langle\exp[-i\mathbf{p}\cdot\mathbf{R}(0)/\hbar]\exp[i\mathbf{p}\cdot\mathbf{R}(t)/\hbar]\rangle_T=\int\exp(i\mathbf{p}\cdot\mathbf{r}/\hbar)G_s(\mathbf{r},t)d\mathbf{r}. \tag{3}$$

The inversion then gives

$$\begin{aligned}G_s(\mathbf{r},t)&=(2\pi)^{-3}\int\exp(-i\mathbf{p}\cdot\mathbf{r}/\hbar)\\
&\quad\times\langle\exp[-i\mathbf{p}\cdot\mathbf{R}(0)/\hbar]\exp[i\mathbf{p}\cdot\mathbf{R}(t)/\hbar]\rangle_T d(\mathbf{p}/\hbar)\\
&=\left\langle\int d\mathbf{r}'\delta[\mathbf{r}+\mathbf{R}(0)-\mathbf{r}']\delta[\mathbf{r}'-\mathbf{R}(t)]\right\rangle_T.\end{aligned} \tag{4}$$

For $t=0$, $G_s(\mathbf{r},0)=\delta(\mathbf{r})$. $G_s(\mathbf{r},t)$ describes the correlation between the position of one and the same particle at different times. It gives, in the classical case, the probability of finding a particle at time t at position $\mathbf{r}$, if the same particle was at the origin at time $t=0$. The interpretation of this function is not quite clear in a quantum mechanical treatment and is discussed in the Appendix. Van Hove[5] has discussed the $G_s(\mathbf{r},t)$ function in detail and we shall refer to his original paper.

From (2) and (3) we have

$$\sigma_a(E)=\frac{\sigma_0\Gamma}{4\hbar}\int\exp[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)-(\Gamma/2\hbar)|t|]\times G_s(\mathbf{r},t)d\mathbf{r}dt, \tag{5}$$

where $\hbar\omega=E-E_0$, $\hbar\boldsymbol{\kappa}=\mathbf{p}$.

As shown by Van Hove,[5] the incoherent differential scattering cross section for slow neutrons is proportional to the integral in (5) with $\Gamma=0$. In Lamb's theory,[3] the probability of resonance absorption of neutrons of energy E is also given by Eq. (1) besides a constant factor and is, therefore, proportional to the integral in (5). Thus the relevant term in the cross section for all the three processes—resonance absorption of neutron and γ rays by nuclei and neutron scattering (with $\Gamma=0$) is given by an expression of the type (5). We shall see in the sequel that the cross section for the

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[4] W. Heitler, *The Quantum Theory of Radiation* (Oxford University Press, New York, 1944), 2nd ed., p. 110.

[5] L. Van Hove, Phys. Rev. **95**, 249 (1954). See also R. J. Glauber, Phys. Rev. **98**, 1092 (1955).

resonance absorption of γ rays by nuclei whether in a gas or bound in a solid or a liquid will follow from (5) depending on the explicit form of $G_s(\mathbf{r},t)$. It is possible to calculate the function $G_s(\mathbf{r},t)$ rigorously in the case of a Maxwellian gas and in the case of a solid in the harmonic approximation but it is not possible to do so in the case of a liquid. Nevertheless, in the latter case one could use in an approximate way the classical form of $G_s(\mathbf{r},t)$; e.g., the solution of the usual diffusion equation or better the solution of Langevin's equation for Brownian motion. The behavior of $G_s(\mathbf{r},t)$ for very small and very large times is known and for intermediate values of the time one could try different forms of $G_s(\mathbf{r},t)$ so as to fit the experimental data. Thus, a general formulation of the absorption probability (the same holds for emission) in terms of the self-correlation function $G_s(\mathbf{r},t)$ as expressed by Eq. (5), has a definite advantage.

It has been shown by Van Hove[5] that the self-correlation function in the case of a gas or a solid (cubic symmetric crystals) has the general form

$$G_s(\mathbf{r},t)=[2\pi\gamma(t)]^{-\frac{3}{2}}\exp[-r^2/2\gamma(t)]. \tag{6}$$

There is no obvious reason to believe that in the case of a liquid $G_s(\mathbf{r},t)$ has also the above general form. It seems, however, reasonable to assume that (6) is a good approximation for a liquid too. We know that it is correct for small as well as large times.

The probability $w_e(E)$ for the emission of a γ ray is also given by Eq. (1) except that the signs of ϵ_n and ϵ_{n0} are interchanged and the constant is different.[4] Proceeding as before, it is easy to show that $w_e(E)$ is given by

$$w_e(E)=\frac{1}{2\pi\hbar}\int\exp[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)-(\Gamma/2\hbar)|t|]\times G_s(\mathbf{r},-t)d\mathbf{r}dt. \tag{7}$$

It is normalized such that $\int_0^\infty w_e(E)dE=1$.

The quantity of experimental interest is the self-absorption cross section σ which for a thin absorber is defined by

$$\sigma=\int_0^\infty\sigma_a(E)w_e(E)dE\bigg/\int_0^\infty w_e(E)dE=\int_0^\infty\sigma_a(E)w_e(E)dE. \tag{8}$$

In a γ-ray resonance absorption experiment if the emitter is made to move with velocity v relative to the absorber, the emitted γ ray gets an energy Doppler shift $s=(v/c)E_0$, c being the velocity of light, and in that case the argument of $\sigma_a(E)$ should be replaced by $s+E$. If we do this and make use of (5), (6), and (7) in (8), it follows that the self-absorption cross section is given by, noticing that the integration over E can be extended to $-\infty$ without any appreciable error,

$$\sigma(s)=\frac{\sigma_0\Gamma}{4\hbar}\int\exp\left(-\frac{its}{\hbar}-\frac{\Gamma}{\hbar}|t|\right)\times\exp\left\{-\frac{\kappa^2}{2}[\gamma_e(t)+\gamma_a(t)]\right\}dt. \tag{9}$$

And if the emitter and the absorber are identical (9) becomes

$$\sigma(s)=\tfrac{1}{2}\sigma_a(s), \tag{10}$$

where $\sigma_a(s)$ is given by (5) with Γ replaced by 2Γ and $\gamma(t)$ replaced by $2\gamma(t)$. Before we proceed to calculate $\sigma(s)$ for a nucleus bound in a solid, we shall evaluate the absorption cross section $\sigma_a(E)$ for a nucleus in a perfect gas.

ABSORPTION OF A γ RAY BY AN ATOM IN A PERFECT GAS

It has been shown by Van Hove[5] that for a perfect gas the quantum mechanical form of $G_s(\mathbf{r},t)$ is the one given by (6) with

$$\gamma(t)=-i\frac{\hbar t}{M}+\frac{k_BTt^2}{M}, \tag{11}$$

where M is the mass of the atom and k_B is the Boltzmann's constant, and T is the temperature of the gas. The term linear in t is purely of quantum mechanical origin and the term quadratic in t survives in the classical limit. Vineyard[6] has shown that for very small times for an arbitrary interacting system described by a time-independent Hamiltonian $\gamma(t)$ is given by

$$\gamma(t)=-i\frac{\hbar t}{M}+\frac{1}{3M^2}\langle\mathbf{p}^2\rangle_T t^2, \tag{12}$$

where $\mathbf{p}$ is the momentum operator of an atom. This result easily follows from (3) if we expand the operator $\mathbf{R}(t)$ in powers of t and define $\gamma(t)$ by the relation

$$\gamma(t)=\frac{1}{3}\int r^2G_s(\mathbf{r},t)d\mathbf{r},$$

and assume that the system is isotropic.

Substituting (11) in (6) and using the resulting $G_s(\mathbf{r},t)$ in (5) and after performing integration over $\mathbf{r}$ we have

$$\sigma_a(E)=\frac{\sigma_0\Gamma}{4\hbar}\int_{-\infty}^{\infty}\exp\left[-\frac{it}{\hbar}(E-E_0-R)-\frac{\Gamma}{2\hbar}|t|-\frac{\Delta^2t^2}{4\hbar^2}\right]dt, \tag{13}$$

where we have put

$$R\text{ (the recoil energy)}=\hbar^2\kappa^2/2M=E_0^2/2Mc^2,\quad \Delta=2(Rk_BT)^{\frac{1}{2}}. \tag{14}$$

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[6] G. H. Vineyard, Phys. Rev. **110**, 999 (1958).

Putting $y = t\Gamma/2\hbar$ and making use of the convolution formula for the Fourier transform of a product, we have

$$\sigma_a(E) = \frac{\sigma_0}{2}\int_{-\infty}^{\infty} dz$$
$$\times\left\{\frac{1}{(2\pi)^{\frac{1}{2}}}\int_{-\infty}^{\infty} \exp\left[-iyz - iy\frac{(E-E_0-R)}{\Gamma/2} - y^2\frac{\Delta^2}{\Gamma^2}\right]dy\right\}$$
$$\times\left\{\frac{1}{(2\pi)^{\frac{1}{2}}}\int_{-\infty}^{\infty} \exp(iy'z - |y'|)dy'\right\},$$

which gives

$$\sigma_a(E) = \sigma_0\frac{\xi}{2\sqrt{\pi}}\int_{-\infty}^{\infty}\frac{dz}{1+z^2}\exp[-\tfrac{1}{4}\xi^2(z+x)^2], \quad (15)$$

where

$$x = \frac{E-E_0-R}{\Gamma/2}; \quad \xi = \frac{\Gamma}{\Delta}. \quad (16)$$

Formula (15) is the same as given by Bethe and Placzek[7] in the case of resonance capture of neutrons by atoms forming a Maxwellian gas.

RESONANCE ABSORPTION OF γ RAYS BY ATOMS IN A CRYSTAL

We shall here restrict ourselves to cubic Bravais lattices. Again Van Hove[5] has shown that for a monoatomic cubic crystal $\gamma(t)$ is given by

$$\gamma(t) = \frac{\hbar^2}{M}\int_0^{\infty}\left[\coth\left(\frac{z}{2k_BT}\right)\left(1-\cos\frac{zt}{\hbar}\right) - i\sin\frac{zt}{\hbar}\right]\frac{f(z)}{z}dz, \quad (17)$$

where $f(z)$ is the distribution of energy levels of the phonons and such that

$$\int_0^{\infty} f(z)dz = 1.$$

$f(z)$ is zero beyond $z = z_{\max}$.

Equation (5) with the help of (6) can be written after integration over r as

$$\sigma_a(E)$$
$$= \frac{\sigma_0\Gamma}{4\hbar}\left\{\exp[-\tfrac{1}{2}\kappa^2\gamma(\infty)]\int_{-\infty}^{\infty}\exp\left(-i\omega t - \frac{\Gamma}{2\hbar}|t|\right)dt\right.$$
$$+\exp[-\tfrac{1}{2}\kappa^2\gamma(\infty)]\int_{-\infty}^{\infty}\exp\left(-i\omega t - \frac{\Gamma}{2\hbar}|t|\right)$$
$$\left.\times\{\exp[\tfrac{1}{2}\kappa^2(\gamma(\infty)-\gamma(t))]-1\}dt\right\},$$

where $\gamma(\infty)$ is the value of $\gamma(t)$ at $t = \infty$. The exponential within the square brackets can now be expanded in a power series, and we have

$$\sigma_a(E) = 2\pi\frac{\sigma_0\Gamma}{4\hbar}\exp(-2W)\left\{\frac{\hbar\Gamma}{2\pi}\frac{1}{(E-E_0)^2+\Gamma^2/4} + \sum_{n=1}^{\infty}\frac{(\kappa^2/2)^n}{n!}\frac{1}{2\pi}\int_{-\infty}^{\infty}\exp\left(-i\omega t - \frac{\Gamma}{2\hbar}|t|\right)[\gamma(\infty)-\gamma(t)]^n dt\right\}$$
$$= \frac{\pi\sigma_0\Gamma}{2}\left[\frac{\Gamma}{2\pi}\frac{1}{(E-E_0)^2+\Gamma^2/4} + \sum_{n=1}^{\infty}\frac{(2W)^n}{n!}g_n(E-E_0, T)\right]\exp(-2W), \quad (18)$$

since Γ can be neglected in the integrand in Eq. (18), and where

$$g_1(E,T) = \frac{f(|E|)}{2EF(T)}\left[\coth\left(\frac{E}{2k_BT}\right) - 1\right], \quad (19)$$

$$g_n(E,T) = \int_{-\infty}^{\infty} g_1(E-E', T)g_{n-1}(E',T)dE', \quad (20)$$

$$F(T) = \int_0^{\infty}\frac{f(z)}{z}\coth\left(\frac{z}{2k_BT}\right)dz, \quad (21)$$

and

$$2W = \tfrac{1}{2}\kappa^2\gamma(\infty) = \frac{\hbar^2\kappa^2}{2M}F(T). \quad (22)$$

$2W$ is the usual Debye-Waller factor. The above formulation is the same as that used by Sjölander[8] in connection with neutron scattering by solids. It is instructive to compare formula (18) with that for the incoherent differential scattering cross section for neutrons in solids. The first term inside the curly brackets gives a sharp absorption peak of width Γ and represents the recoilless absorption of γ rays, and corresponds to elastic scattering in the neutron case (where it is a delta function). The other terms give a broad peak extending at least over an energy $z_{\max}$ and corresponds to phonon exchange.

In the Debye approximation,

$$\begin{aligned} f(z) &= 3z^2/(k_B\Theta)^3 && \text{for } z \le k_B\Theta \\ &= 0 && \text{for } z > k_B\Theta, \end{aligned} \quad (23)$$

Θ being the Debye temperature of the solid. Using (23) in (21) it is easy to show that

$$F(T) = \frac{6}{k_B\Theta}\left[\frac{1}{4} + \frac{T}{\Theta}\phi\left(\frac{\Theta}{T}\right)\right], \quad (24a)$$

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[7] H. Bethe and G. Placzek, Phys. Rev. **51**, 462 (1937).

[8] A. Sjölander, Arkiv Fysik **14**, 315 (1958).

where

$$\phi(z)=\frac{1}{z}\int_0^z \frac{ydy}{e^y-1}.$$

The function $\phi(z)$ has been tabulated by Zener.[9] Now

$$\begin{aligned} F(T)&=3/(2k_B\Theta) && \text{for} \quad T\ll\Theta \\ &=6T/(k_B\Theta^2) && \text{for} \quad T\gg\Theta. \end{aligned} \tag{24b}$$

We also notice that

$$\int_{-\infty}^{\infty} g_n(E)dE=1.$$

Experimentally we are interested in the self-absorption cross section; i.e., in $\sigma(s)$ given by (9). Here the emitter and the absorber are assumed to be of the same material but at different temperatures, say T_e and T_a, respectively. Let v be the relative velocity of the emitter and absorber. $s=(v/c)E_0$ is positive if the two move towards each other and negative if they move away from each other. Proceeding as before, it follows from (9) that

$$\sigma_a(s)=\frac{\pi\sigma_0\Gamma}{2}e^{-(2W_e+2W_a)} \times\left[\frac{\Gamma}{\pi}\frac{1}{s^2+\Gamma^2}+\sum_{n=1}^{\infty}\frac{(2W_e+2W_a)^n}{n!}\bar{g}_n(s)\right], \tag{25}$$

where

$$2W_e=(\hbar^2\kappa^2/2M)F(T_e),$$

$$2W_a=(\hbar^2\kappa^2/2M)F(T_a),$$

$$\bar{g}_1(s)=\frac{1}{F(T_e)+F(T_a)} \times[F(T_e)g_1(s,T_e)+F(T_a)g_1(s,T_a)], \tag{26}$$

$$\bar{g}_n(s)=\int_{-\infty}^{\infty}\bar{g}_1(s-s')\bar{g}_{n-1}(s')ds'.$$

It should be borne in mind that the energy distribution of the phonons changes with temperature and hence the Debye temperature also changes. There will be a very slight shift of the resonance absorption peak due to the fact that when a γ ray is emitted or absorbed the mass of the emitting or the absorbing nucleus changes. This second order Doppler effect[10] has not been considered here.

If the emitter and the absorber are both identical and are at the same temperature, Eq. (25) simplifies to

$$\sigma(s)=\frac{\pi\sigma_0\Gamma}{2}e^{-4W}\left[\frac{\Gamma}{\pi}\frac{1}{s^2+\Gamma^2}+\sum_{n=1}^{\infty}\frac{(4W)^n}{n!}g_n(s,T)\right]. \tag{27}$$

The first term in (27) gives a sharp resonance peak having a full width 2Γ. For $s=0$, the first term is

$$\sigma'(0)=\tfrac{1}{2}\sigma_0e^{-4W}. \tag{28}$$

The resonance self-absorption cross section is thus diminished by a factor e^{-4W}, where $2W$, in the Debye approximation, is given by Eqs. (22) and (24). From the expression for $2W$, it is clear that to have a large Mössbauer effect the recoil energy R of the nucleus must be small; i.e., the γ ray should have a low energy and the Debye temperature Θ of the solid should be large and the temperature as low as possible. Recently Lipkin[11] has derived the expression for $2W$ in a simple manner and has also come to the same conclusions. In the original Mössbauer experiment in which Ir^{191} 129-kev gamma rays were used ($R=0.046$ ev, $k_B\Theta=0.025$ ev, $T=88°\text{K}$), $2W$ was nearly equal to 3; and hence the resonance effect was very small. For a large resonance effect $\sigma'(0)$ has to be greater than the non-nuclear cross section such as the cross section for the photoelectric effect. Unfortunately for isotopes so far investigated, the Mössbauer effect is very small except in the case of Fe^{57}, where because of the low γ-ray energy ($E_0=14.4$ kev), $2W$ is nearly 0.1 at $T=0°\text{K}$, and this is the reason why it is possible to observe the Mössbauer effect even at very high temperatures. Because of this comparatively large effect and the extreme sharpness of the resonance line ($\Gamma\sim5\times10^{-9}$ ev), the Mössbauer effect in Fe^{57} nucleus has found recently so many interesting applications.

The second term in (27), corresponding to phonon exchange, gives the shape of the wings of the sharp resonance absorption line; the wings extending at least up to an energy of the order $k_B\Theta$. If $2W\ll1$, all terms except the first in the sum are negligible. In that case the shape of the wings is related in a very simple way through Eq. (19) to the energy spectrum $f(E)$ of the crystal vibrations. It is thus at least in principle possible to measure the energy distribution function of the phonons as has been pointed out earlier by Visscher.[12] In this connection it is important to realize that if the nucleus emitting the γ rays constitutes a foreign atom in a host lattice, what one measures is not the vibrational spectrum of the host lattice but a spectrum which is characteristic of the local surroundings of the emitting nucleus. In addition to this, the one-phonon cross section is very small and this limits the possibility of using the Mössbauer effect to investigate the vibrational spectra of solids. A better way to study the real vibrational spectra is through the use of slow neutron scattering.

If $2W\gg1$, then we have what is called the weak-binding case. For example in the original Mössbauer experiment $2W\simeq3$ and it falls under this category.

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[9] C. Zener, Phys. Rev. **49**, 122 (1936).

[10] B. D. Josephson, Phys. Rev. Letters **4**, 341 (1960).

[11] H. Lipkin, Ann. Phys. **9**, 332 (1960).

[12] W. M. Visscher, Ann. Phys. **9**, 194 (1960).

From (17) it follows that

$$\tfrac{1}{2}\kappa^2[\gamma_e(t)+\gamma_a(t)]$$

$$=-i2R\frac{t}{\hbar}+2\Delta^2\frac{t^2}{4\hbar^2}+\cdots \quad \text{for} \quad t\ll\frac{\hbar}{k_B\Theta} \tag{29a}$$

$$=R[F(T_e)+F(T_a)] \quad \text{for} \quad t\gg\frac{\hbar}{k_B\Theta}, \tag{29b}$$

where

$$\Delta^2=(8/3)R(E_{\text{kin}}{}^e+E_{\text{kin}}{}^a). \tag{30}$$

E_{kin} is the mean kinetic energy per atom and is given by

$$E_{\text{kin}}=\frac{3}{4}\int_0^\infty z\coth\left(\frac{z}{2k_BT}\right)f(z)dz.$$

For $T>\Theta$, $E_{\text{kin}}\approx\frac{3}{2}k_BT$.

Now Eq. (9) can be written as

$$\sigma(s)=\frac{\sigma_0\Gamma}{4\hbar}\left\{\int_{-\tau}^{\tau}+\int_{-\infty}^{-\tau}+\int_{\tau}^{\infty}\right\}dt$$
$$\times\exp\left\{-i\frac{ts}{\hbar}-\frac{\Gamma}{\hbar}|t|-\frac{\kappa^2}{2}[\gamma_e(t)+\gamma_a(t)]\right\}, \tag{31}$$

where $\tau\sim\hbar/k_B\Theta$.

In (31) the exponent $\frac{1}{2}\kappa^2[\gamma_e(t)+\gamma_a(t)]$ in the first integral can be replaced by (29a), and in the second and third integrals by (29b), without introducing appreciable error. It is then easy to show that

$$\sigma(s)=\frac{\sigma_0\Gamma}{4\hbar}\left\{\int_{-\infty}^{\infty}\exp\left[-\frac{it}{\hbar}(s-2R)-\frac{\Gamma}{\hbar}|t|-\frac{2\Delta^2}{4\hbar^2}t^2\right]dt\right.$$
$$\left.+\frac{2\hbar\Gamma}{s^2+\Gamma^2}\exp(-2W_e-2W_a)\right\}. \tag{32}$$

The integral in (32) is the same as the one which occurs in (13) and can be evaluated as before. Hence

$$\sigma(s)=\frac{\sigma_0\Gamma^2}{2}\frac{\exp-(2W_e+2W_a)}{s^2+\Gamma^2}$$
$$+\sigma_0\frac{\xi}{4\sqrt{\pi}}\int_{-\infty}^{\infty}\frac{dz}{1+z^2}\exp[-\tfrac{1}{4}\xi^2(x+z)^2], \tag{33}$$

where we have defined

$$\xi=2\Gamma/\Delta,\quad \Delta^2=(8/3)R(E_{\text{kin}}{}^e+E_{\text{kin}}{}^a)=\Delta_e{}^2+\Delta_a{}^2,$$
$$x=(s-2R)/\Gamma,\quad R=E_0{}^2/2Mc^2. \tag{34}$$

If $\xi\ll1$; i.e., the linewidth Γ is much smaller than the Doppler width Δ Eq. (33) for $s=0$ simplifies to

$$\sigma(0)=\frac{\sigma_0}{2}\exp(-2W_e-2W_a)$$
$$+\frac{\sigma_0\sqrt{\pi}}{2}\frac{\Gamma}{(\Delta_e{}^2+\Delta_a{}^2)^{\frac{1}{2}}}\exp\left[-\frac{4R^2}{\Delta_e{}^2+\Delta_a{}^2}\right]. \tag{35}$$

Equation (35) is the same as the formula (19) of Mössbauer.[13]

DIFFUSION BROADENING OF THE RESONANCE LINE

In this section we shall show how Mössbauer technique could be used to investigate the nature of diffusive motions in solids and probably under more favorable circumstances in a liquid too. In a solid the slow jumping movement of an atom from one lattice site to another gives rise to a broadening of the resonance line. At ordinary temperatures the broadening due to such a diffusive motion is small compared to the natural linewidth but at elevated temperatures the former can become of the same order of magnitude as the latter and even greater. In liquids the diffusive broadening is, however, many orders of magnitude greater than the linewidth but, unfortunately, the resonance absorption cross section is in most cases small compared to non-nuclear absorption cross section. This makes it difficult to distinguish the resonance line from the background.

The self-correlation function $G_s(\mathbf{r},t)$ as defined by Eq. (3) is a complex quantity and cannot, therefore, easily be interpreted as a self-diffusion function except in the case that its imaginary part is negligible. The imaginary part, as we know, is quantum mechanical in origin. It is, however, possible as Schofield[14] has done to define a real function which in the classical case goes over to the classical self-diffusion function and which is related to the absorption cross section in a similar way as is Van Hove's $G_s(\mathbf{r},t)$ function. The transformation suggested by Schofield and the question of using the real part of the Van Hove's $G_s(\mathbf{r},t)$ function are discussed in detail in the Appendix of this paper. Such a discussion besides being relevant to the context of this paper is of importance in connection with neutron scattering by liquids.

Following the suggestion of Schofield, if we replace t by $t+(i\hbar/2k_BT)$, $G_s(\mathbf{r},t)$ goes over to $F_s(\mathbf{r},t)$, which is given by (8A) of the Appendix and $\gamma(t)$ goes over to $\rho(t)$, where $\rho(t)$ is given by Eqs. (9A) and (10A) of the Appendix in the case of a gas and a solid, respectively. In the Appendix we have derived the expression for the resonance absorption cross section $\sigma_a(E)$ and for the emission probability $w_e(E)$, which are, respectively, given by Eqs. (11A) and (12A). We shall rewrite them

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[13] R. L. Mössbauer, Z. Physik **151**, 124 (1958).

[14] P. Schofield, Phys. Rev. Letters **4**, 239 (1960).

here

$$\sigma_a(E)=\frac{\sigma_0\Gamma}{4\hbar}\exp\left[\frac{\hbar\omega}{2k_BT}-\frac{\hbar^2\kappa^2}{8Mk_BT}\right]\times\int_{-\infty}^{\infty}\exp\left[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)-\frac{\Gamma}{2\hbar}|t|\right]\times F_s{}^c(\mathbf{r},t)d\mathbf{r}dt, \qquad (36)$$

$$w_e(E)=\frac{1}{2\pi\hbar}\exp\left[-\frac{\hbar\omega}{2k_BT}-\frac{\hbar^2\kappa^2}{8Mk_BT}\right]\times\int_{-\infty}^{\infty}\exp\left[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)-\frac{\Gamma}{2\hbar}|t|\right]\times F_s{}^c(\mathbf{r},t)d\mathbf{r}dt, \qquad (37)$$

where $F_s{}^c(\mathbf{r},t)$ is the classical self-diffusion function and $\hbar\omega=E-E_0$.

We shall consider two simple cases: (i) in which the diffusive motion of an atom in the absorber is governed by the simple diffusion equation, and (ii) in which the atom jumps from one lattice site to another. Diffusion in normal liquids probably comes under case (i) whereas in solids it comes under case (ii). These two cases are considered here more as illustrations rather than to give a precise relationship between the resonance line shape and diffusive motions.

Case (i)

In this case $F_s{}^c(\mathbf{r},t)$ is given by

$$F_s{}^c(\mathbf{r},t)=(4\pi D|t|)^{-\frac{3}{2}}\exp(-r^2/4D|t|), \qquad (38)$$

where D is the diffusion coefficient. This function has the right limiting form for large t but not for $t\rightarrow 0$. One should rather use for $F_s{}^c(\mathbf{r},t)$ the solution of Langevin's equation for the Brownian motion with $\rho(t)$ as given by (13A). $\rho(t)$ varies as t^2 for $t\rightarrow 0$. We shall not use the latter form of $\rho(t)$ since the change in the linewidth as a result of this refinement is negligible (see Singwi and Sjölander[15] in connection with neutron scattering).

Let us suppose that the absorber is in the liquid state. The cross section for the absorption of a γ ray of energy E is obtained by substituting (38) in (36) and after performing the integrations we have

$$\sigma_a(E)=(\sigma_0\Gamma/4)\exp(-2W_a)(\Gamma+2\hbar\kappa^2D)/[(E-E_0)^2+\tfrac{1}{4}(\Gamma+2\hbar\kappa^2D)^2], \qquad (39)$$

where in deducing (39) we have replaced

$$\exp[-(E-E_0)/2k_BT]$$

by unity, since $E-E_0\ll 2k_BT$ in the resonance peak and where we have put $\hbar^2\kappa^2/8Mk_BT=2W_a$. $2W_a$ is analogous to the Debye-Waller factor in the case of a solid.

From (39) it is evident that the broadening $\Delta\epsilon$ of the resonance line due to diffusion is given by

$$\Delta\epsilon=2\hbar\kappa^2D=2E_0{}^2D/\hbar c^2, \qquad (40)$$

where E_0 is the energy of the γ ray and c is the velocity of light. As an example let us take iron for which $D\sim 10^{-5}$ cm^2/sec in the molten state, and $E_0=14$ kev (for Fe^{57}). Equation (40) gives $\Delta\epsilon\simeq 6\times 10^{-3}$ ev which is several orders of magnitude greater than the natural width Γ.

Experimentally what one measures is the self-absorption cross section

$$\sigma(s)=\int_0^{\infty}w_e(E)\sigma_a(E+s)dE.$$

Here $w_e(E)$ is the emission probability in the case of a solid, since the emitter is in the form of a solid. If we neglect the phonon part, the expression for $w_e(E)$ is

$$w_e(E)=\frac{\Gamma}{2\pi}e^{-2W_e}\frac{1}{(E-E_0)^2+\Gamma^2/4}. \qquad (41)$$

Using (39) and (41) in the expression for $\sigma(s)$, we get

$$\sigma(s)=\frac{\sigma_0\Gamma}{2}\exp(-2W_e-2W_a)\frac{\Gamma+\hbar\kappa^2D}{s^2+(\Gamma+\hbar\kappa^2D)^2}. \qquad (42)$$

Recently a cold-neutron scattering method has been used to measure the diffusive broadening of the "quasi-elastic" scattering in liquids.[16–18] This method, unfortunately, suffers from the disadvantage of having a poor energy resolution. But if we were to study the diffusive broadening by Mössbauer technique, such a disadvantage does not exist since the natural width of the line is negligible compared to the diffusive broadening. However, this method seems at present to be hardly practicable because of the smallness of $\sigma(s)$ compared to the other non-nuclear cross section such as the photoelectric effect. But under very favorable circumstances such that $\Gamma/\Delta\epsilon$ is not too small this method could be used to investigate the shape of the resonance line and determine the diffusion coefficient from the measurement of line broadening.

Case (ii)

Let τ_0 be the mean time for which an atom stays on a given lattice site before jumping to a new lattice position. If we now assume that there is no correlation in motion between one jump and the next, it is possible

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

[16] B. N. Brockhouse, Phys. Rev. Letters **2**, 287 (1959).

[17] D. J. Hughes, H. Palevsky, W. Kley, and E. Tunkelo, Phys. Rev. Letters **3**, 91 (1959).

[18] I. Pelah, W. L. Whittemore, and A. W. McReynolds, Phys. Rev. **113**, 767 (1959).

to calculate $F_s^c(\mathbf{r},t)$ or rather its Fourier transform as has been done earlier by Singwi and Sjölander[15] in connection with diffusive motions in water and cold-neutron scattering. The problem under consideration is in fact a special case of the more general formula of Singwi and Sjölander. The present case consists in taking $\tau_1 \rightarrow 0$, where τ_1 is the mean time for which the particle diffuses between its two oscillatory states and in taking the function $h(r,t)$ to be independent of time. It is then easy to show by the use of formula (36) that

$$\sigma_a(E)=\frac{\sigma_0\Gamma}{4}\exp(-2W_a)\times\frac{\Gamma+(2\hbar/\tau_0)(1-\alpha)}{(E-E_0)^2+[\Gamma+(2\hbar/\tau_0)(1-\alpha)]^2/4}, \tag{43}$$

where

$$\alpha=\int\exp(i\boldsymbol{\kappa}\cdot\mathbf{r})h(\mathbf{r})d\mathbf{r}, \tag{44}$$

$h(\mathbf{r})$ gives the probability of finding the particle at the position $\mathbf{r}$ after a single jump, if the particle was at the origin before the jump. Using (43) and (41) we have for the self-absorption cross section

$$\sigma(s)=\frac{\sigma_0\Gamma}{2}\exp(-2W_e-2W_a)\times\frac{\Gamma+(\hbar/\tau_0)(1-\alpha)}{s^2+[\Gamma+(\hbar/\tau_0)(1-\alpha)]^2}. \tag{45}$$

The diffusion coefficient D is defined by

$$D=\frac{1}{6\tau_0}\int r^2h(\mathbf{r})d\mathbf{r}. \tag{46}$$

From formula (43) it is clear that the broadening $\Delta\epsilon$ of the resonance peak due to diffusive motions is

$$\Delta\epsilon=2\hbar/\tau_0\left[1-\int\exp(i\boldsymbol{\kappa}\cdot\mathbf{r})\ h(\mathbf{r})d\mathbf{r}\right]. \tag{47}$$

We thus see that the maximum value of the broadening is $2\hbar/\tau_0$ and the broadening depends on the angle between the direction of motion of the diffusing atom and the direction of the γ-ray quantum. Consider a Fe^{57} nucleus sandwiched between two layers of a graphite lattice (it is possible to introduce iron atoms between the layer planes of a graphite single crystal). The Fe^{57} nucleus finds it hard to move in the direction of the c-axis but can diffuse with ease in the basal plane. If the γ ray from the emitter falls on the absorber parallel to the c axis and the counter is also pointing along the c axis, the diffusive broadening $\Delta\epsilon$ in this case will be negligible and the resonance line will have its natural width. If we now rotate the absorber relative to the direction of the incident γ ray, the diffusive broadening should increase. At the same time the magnitude of the resonance absorption would decrease due to the anisotropy of the Debye-Waller factor (our formulas can easily be extended for an anisotropic solid).

Let us consider self-diffusion in iron. The emitter is at low temperature and the resonance absorption is studied as a function of the velocity of the emitter for various temperatures of the absorber. At ordinary temperatures, the self-diffusion in iron is so small that the line broadening due to diffusive motion is negligible compared to the natural width Γ. For example even at 760°C, the diffusion coefficient is only 1.5×10^{-12} cm^2/sec, which would give a value of 6×10^{-5} sec for τ_0; since $\tau_0 \simeq l^2/6D$, l being the interatomic spacing. This would correspond to a broadening $(\Delta_b)_{\max}\simeq 2\times10^{-11}$ ev, whereas $\Gamma=4.6\times10^{-9}$ ev. However, at higher temperatures, say 1000°C and above, it should be possible to detect the diffusive broadening by a Mössbauer-type experiment. At such high temperatures the Debye-Waller factor e^{-2W_a} (since $2W_e \ll 2W_a$) would no doubt decrease but it is still not too small ($\sim e^{-3}$) as to preclude the possibility of observing the resonance effect.

It has been reported[19] that the rate of self-diffusion in iron at 757°C, under plastic deformation, increases by as much as a factor of thousand.[20] And if it is true, the line broadening due to diffusion would now be nearly 2×10^{-8} ev which is greater than the natural line-width and it might, therefore, be possible to detect it by a Mössbauer-type experiment. It would be valuable to perform such an experiment in view of the fact that there exists a controversy between different experimental workers regarding the enhancement of the self diffusion and the range of temperature for which it is significant. Besides a Mössbauer-type experiment is different from the usual diffusion experiments using tracers and should, therefore, provide an independent check. One could also study the impurity diffusion of iron in other metals like copper and silver. Such an experiment would give a direct measure of the mean time τ_0 and its temperature variation.

APPENDIX

The function $G_s(\mathbf{r},t)$ as defined by Eq. (3) could only in the classical limit be interpreted as the self-diffusion function. For small times when the particle under consideration has moved only a distance of the order of the de Broglie wavelength, quantum effects are important and $G_s(\mathbf{r},t)$ is complex. In fact, according to Van Hove[5] it is only the real part of $G_s(\mathbf{r},t)$ which has the above physical interpretation. It is, however, possible to express the emission or the absorption probability in terms of the real part of $G_s(\mathbf{r},t)$.

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[19] N. Ujiive, B. Averbach, M. Cohen, and V. Griffiths, Acta Met. **6**, 68 (1958).

[20] For a general discussion see the review article by D. Lazarus, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1960), Vol. 8, p. 71.

Now

$$\frac{1}{2\pi}\int_{-\infty}^{\infty}\exp(-i\omega t)\langle\exp[-i\boldsymbol{\kappa}\cdot\mathbf{R}(0)]\exp[i\boldsymbol{\kappa}\cdot\mathbf{R}(t)]\rangle_T dt$$
$$=\sum\nolimits_{n,n0}g_{n0}|\langle n|\exp(i\boldsymbol{\kappa}\cdot\mathbf{R})|n_0\rangle|^2$$
$$\times\delta[\omega-(\epsilon_n-\epsilon_{n0})/\hbar],\quad(1\text{A})$$

which follows from the definition of $\langle\cdots\rangle_T$ and $g_{nn0}=\exp(-E_{n0}/k_BT)/\sum_n\exp(-E_n/k_BT)$. Further

$$\frac{1}{2\pi}\int_{-\infty}^{\infty}\exp(-i\omega t)\langle\exp[-i\boldsymbol{\kappa}\cdot\mathbf{R}(t)]\exp[i\boldsymbol{\kappa}\cdot\mathbf{R}(0)]\rangle_T dt$$
$$=\sum\nolimits_{n,n0}g_{n0,}|\langle n|\exp(i\boldsymbol{\kappa}\cdot\mathbf{R})|n0\rangle|^2\delta[\omega+(\epsilon_n-\epsilon_{n0})/\hbar]$$
$$=\sum\nolimits_{n,n0}g_{n0}|\langle n0|\exp(i\boldsymbol{\kappa}\cdot\mathbf{R})|n\rangle|^2\delta[\omega-(\epsilon_n-\epsilon_{n0})/\hbar]$$
$$=e^{-\beta\hbar\omega}\sum\nolimits_{n,n0}g_{n0}|\langle n|\exp(i\boldsymbol{\kappa}\cdot\mathbf{R})|n0\rangle|^2$$
$$\times\delta[\omega-(\epsilon_n-\epsilon_{n0})/\hbar]$$
$$=e^{-\beta\hbar\omega}\frac{1}{2\pi}\int_{-\infty}^{\infty}\exp(-i\omega t)$$
$$\times\langle\exp[-i\boldsymbol{\kappa}\cdot\mathbf{R}(0)]\exp[i\boldsymbol{\kappa}\cdot\mathbf{R}(t)]\rangle_T dt.\quad(2\text{A})$$

The last step in (2A) follows from (1A). The relation $g_n=\exp[-\beta(\epsilon_n-\epsilon_{n0})]g_{n0}$ has been used in the second step in (2A); $\beta=1/k_BT$.

Introducing the real part of $G_s(\mathbf{r},t)$, which is defined by

$$\mathrm{Re}[G_s(\mathbf{r},t)]=(2\pi)^{-3}\int\exp(-i\boldsymbol{\kappa}\cdot\mathbf{r})$$
$$\times\tfrac{1}{2}\{\langle\exp[-i\boldsymbol{\kappa}\cdot\mathbf{R}(0)]\exp[i\boldsymbol{\kappa}\cdot\mathbf{R}(t)]$$
$$+\exp[-i\boldsymbol{\kappa}\cdot\mathbf{R}(t)]\exp[i\boldsymbol{\kappa}\cdot\mathbf{R}(0)]\rangle_T\}d\boldsymbol{\kappa},\quad(3\text{A})$$

and using (1A) and (2A) in Eq. (5) of the text we get the following expression for the absorption cross section:

$$\sigma_a(E)=\frac{\sigma_0\Gamma}{4\hbar}\frac{\exp(\beta\hbar\omega/2)}{\cosh(\beta\hbar\omega/2)}$$
$$\times\int\exp[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)-(\Gamma/2\hbar)|t|]$$
$$\times\mathrm{Re}[G_s(\mathbf{r},t)]d\mathbf{r}dt,\quad(4\text{A})$$

considering that $\Gamma\ll k_BT$.

Recently Schofield[14] has also suggested in connection with neutron scattering that $G_s(\mathbf{r},t+i\hbar/2k_BT)$ rather than $G_s(\mathbf{r},t)$ should be considered as a self-diffusion function. He points out that if, for instance, $G_s(\mathbf{r},t)$ is replaced by its classical equivalent obtained from the simple diffusion equation, as suggested by Vineyard,[6] the scattering cross section will not satisfy the condition of detailed balance. If, however, $G_s(\mathbf{r},t+i\hbar/2k_BT)$ is replaced by the classical self-diffusion function the principle of detailed balance will be satisfied. The same is also true if we replace $\mathrm{Re}[G_s(\mathbf{r},t)]$ in (4A) by its classical equivalent.

Schofield's result is easily obtained by noting that

$$\frac{1}{2\pi}\int_{-\infty}^{\infty}\exp(-i\omega t)\langle\exp[-i\boldsymbol{\kappa}\cdot\mathbf{R}(0)]\exp[i\boldsymbol{\kappa}\cdot\mathbf{R}(t)]\rangle_T dt$$
$$=\sum\nolimits_{n,n0}g_{n0}|\langle n|\exp(i\boldsymbol{\kappa}\cdot\mathbf{R})|n0\rangle|^2\delta[\omega-(\epsilon_n-\epsilon_{n0})/\hbar]$$
$$=\exp(\beta\hbar\omega/2)\sum\nolimits_{n,n0}(g_ng_{n0})^{\frac{1}{2}}|\langle n|\exp(i\boldsymbol{\kappa}\cdot\mathbf{R})|n0\rangle|^2$$
$$\times\delta[\omega-(\epsilon_n-\epsilon_{n0})/\hbar],\quad(5\text{A})$$

and introducing a function

$$F_s(\mathbf{r},t)=(2\pi)^{-3}\int\exp(-i\boldsymbol{\kappa}\cdot\mathbf{r})$$
$$\times\{\sum\nolimits_{n,n0}(g_ng_{n0})^{\frac{1}{2}}\langle n0|\exp[-i\boldsymbol{\kappa}\cdot\mathbf{R}(0)]|n\rangle$$
$$\times\langle n|\exp[i\boldsymbol{\kappa}\cdot\mathbf{R}(t)]|n0\rangle\}d\boldsymbol{\kappa}.\quad(6\text{A})$$

We then have for the absorption cross section

$$\sigma_a(E)=\frac{\sigma_0\Gamma}{4\hbar}\exp(\beta\hbar\omega/2)\int\exp[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)-(\Gamma/2\hbar)|t|]$$
$$\times F_s(\mathbf{r},t)d\mathbf{r}dt.\quad(7\text{A})$$

$F_s(\mathbf{r},t)$ is real and is an even function of t and thus the integral in (7A) is an even function of ω. It is easily shown by using the definition (3) of $G_s(\mathbf{r},t)$ that $F_s(\mathbf{r},t)=G_s(\mathbf{r},t+i\hbar/2k_BT)$. If one uses the classical self-diffusion function instead of $F_s(\mathbf{r},t)$ in (7A) or for $\mathrm{Re}[G_s(\mathbf{r},t)]$ in (4A), the two expressions are identical to the first order in $\hbar\omega/k_BT$.

If we make the transformation as suggested by Schofield, we have

$$F_s(\mathbf{r},t)=[2\pi\rho(t)]^{-\frac{3}{2}}\exp[-r^2/2\rho(t)],\quad(8\text{A})$$

where

$$\rho(t)=\hbar^2/4Mk_BT+(k_BT/M)t^2,\quad(9\text{A})$$

for a free gas, and

$$\rho(t)=(\hbar^2/M)\int_0^{\infty}\frac{f(z)}{z}\tanh(z/4k_BT)dz$$
$$+(\hbar^2/M)\int_0^{\infty}\frac{f(z)}{z}\frac{1-\cos(zt/\hbar)}{\sinh(z/2k_BT)}dz,\quad(10\text{A})$$

for a solid. Equations (9A) and (10A) follow from Eqs. (11) and (17) of the text, respectively.

We notice from (9A) that even at $t=0$, the particle is distributed over a finite region. The finite extension is given by the first term in (9A) and is consistent with Heisenberg's uncertainty principle for a particle with mean velocity $(k_BT/M)^{\frac{1}{2}}$. The real part of $G_s(\mathbf{r},t)$ on the other hand, goes over to a δ function around the origin at $t=0$. It, therefore, appears that $F_s(\mathbf{r},t)$ as given by (8A) is more directly connected with self-diffusion.

Schofield's suggestion, in the case of a liquid, is to replace $F_s(\mathbf{r},t)$ in the first approximation by a classical self-diffusion function obtained, for instance, from Langevin's equation. In that case $\rho(t)$ will go to zero as t^2 for small times and will approach $2D|t|$ for large times. If we, however, add a constant to $\rho(t)$ corresponding to a finite extension of the probability cloud at $t=0$, the resulting formula for the cross section will be valid to some extent also for large momentum transfers.

For a liquid it seems reasonable to take the same constant as that for a gas, since we know that for large momentum transfers corresponding to small times the scattering cross section approximately goes over to a free gas formula. Adding of this constant to $\rho(t)$ will simply amount to multiplying the right-hand side of (7A) by $\exp(-\hbar^2\kappa^2/8Mk_BT)$. In the case of neutron scattering by liquids this factor is often nearly equal to unity except for large incident neutron energy, whereas in the case of γ-ray resonance absorption it could be quite small depending on the recoil energy of the nucleus.

As a result of the foregoing discussion it seems plausible to write (7A) in the form

$$\sigma_a(E)=\frac{\sigma_0\Gamma}{4\hbar}\exp(\hbar\omega/2k_BT-\hbar^2\kappa^2/8Mk_BT)\times\int\exp[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)-(\Gamma/2\hbar)|t|]\times F_s^c(\mathbf{r},t)d\mathbf{r}dt,\qquad(11\text{A})$$

and similarly,

$$w_e(E)=\frac{1}{2\pi\hbar}\exp(-\hbar\omega/2k_BT-\hbar^2\kappa^2/8Mk_BT)\times\int\exp[i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)-(\Gamma/2\hbar)|t|]\times F_s^c(\mathbf{r},t)d\mathbf{r}dt,\qquad(12\text{A})$$

where for $F_s^c(\mathbf{r},t)$ we take the expression (8A) with $\rho(t)$ as given from Langevin's equation, and is[21]

$$\rho(t)=(2D/\beta')[\beta' t-1+\exp(-\beta' t)].\qquad(13\text{A})$$

The characteristic time $1/\beta'$ is given by

$$\beta'=k_BT/DM,\qquad(14\text{A})$$

D being the diffusion coefficient. Of course, this is possible only if the diffusion can really be described by Langevin's equation.

Note added in proof. Recent measurements of the specific heat of indium by Bryant and Keesom [Phys. Rev. Letters **4**, 460 (1959)] and of niobium by Broose *et al.* [Phys. Rev. Letters **5**, 246 (1960)] both in the superconducting and normal phases seem to show that the lattice part of the specific heat is different in the two phases, thus indicating that *perhaps* the phonon spectrum in the two phases is not the same. Broose *et al.*, in an attempt to explain their measurements on niobium have suggested in the superconducting phase an altered value of the Debye temperature as 243°K, which value in the normal state they arrive at is 231°K. Thus, there is a change of five percent in the value of θ_D.

Here we wish to suggest an alternative and perhaps more direct experiment to decide whether there is any appreciable change in the value of θ_D in going from the normal to the superconducting phase. The experiment consists in studying the intensity of the Mössbauer line both in the normal and superconducting phases. The choice for such an experiment is very severely limited to only a few isotopes. The intensity of the Mössbauer line is determined by the Debye-Waller factor e^{-4w}, and in the limit $T\ll\theta_D$, $4w$ is equal to $3R/k_B\theta_D$, where R is the recoil energy. In order to have an appreciable change in the intensity of resonance absorption for a very small change in the value of θ_D, one would demand a large value of $4w$; i.e., a large recoil energy and a small θ_D. Re^{187} is such an example. It becomes superconducting and the values of R and θ_D are, respectively, 0.051 ev and 417°K. An almost trivial calculation will show that a ten percent increase in the value of θ_D will give a 35% increase in the intensity of the resonance absorption, which should be easy to observe. Other isotopes which one could study are Ta^{181} and Hf^{177}.

The authors have been informed privately by Meyer-Schuetzmeister and Hanna that their very preliminary experiment on the Mössbauer effect in Sn, both in the normal and superconducting phases, indicates that there is an increase of a few percent in the intensity of resonance absorption in the latter phase. A five percent increase in the value of θ_D would, in this case, give nearly three percent increase in the intensity.

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[21] See for instance S. Chandrasekhar, Revs. Modern Phys. **15**, 1 (1943).