PHYSICAL REVIEW B VOLUME 12, NUMBER 1 1 JULY 1975

Effect of nuclear motion on Mössbauer relaxation spectra*

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(Received 11 November 1974)

Relaxation effects in Mössbauer line shape are studied when the nucleus jumps from one position to another. Relaxation arises from the fact that the nucleus interacts differently with its surroundings at different sites. At the same time, an additional broadening is observed because of nuclear motion. The effect of surroundings on the nucleus is treated classically in a stochastic-theory model in which it is assumed that the surroundings act like a heat bath and drive thermal fluctuations into the system which cause the nucleus to jump from time to time, from one site to another. But as it jumps to a new site it finds itself in a different quantum-mechanical enviornment. This gives rise to relaxation effects. It is found that nuclear motion precludes the occurrence of motional narrowing of lines which is typical of a pure-relaxation spectrum in the fast-relaxation-rate limit. The Singwi-Sjölander diffusion broadening and the Blume result for pure-relaxation effects are obtained as two limiting cases of the theory. Application of the model to experiment is discussed.

I. INTRODUCTION

Several theoretical calculations and experiments have been done to study relaxation effects in Mössbauer spectra.[1] In all these problems, the Mössbauer nucleus remains stationary; relaxation is caused by fluctuation in its surroundings. Examples are (i) time-dependent magnetic hyperfine interaction due to electronic spin-spin or spin-lattice relaxation; and (ii) randomly changing electric quadrupolar interaction due to Jahn-Teller distortions, interstitial or vacancy diffusion in the vicinity of the Mössbauer nucleus, etc. These relaxation mechanisms typically produce broadening, shift, and finally narrowing of the resonance lines. However, the effect on the relaxation spectra when the nucleus itself is in a state of motion has not been treated so far, albeit there is now experimental evidence of such an effect.[2] It is this situation that we would like to consider in this paper.[3]

There exists a lot of work, theoretical[4] and experimental,[5] on the effect on a Mössbauer line of the motion of the nucleus during the emission or absorption of a γ ray. This motion occurs, due to thermal agitation, in the form of solidlike jump diffusion or gaslike continuous diffusion or a combination of both. In any event, the effect of this nuclear motion is to give rise to a broadening of the resonance line.

The situation that we discuss in this paper occurs when the Mössbauer nucleus, due to its diffusive motion, jumps into a new environment. A new environment means a new Hamiltonian for the nucleus which produces relaxation of the resonance lines. On the other hand, the diffusive motion itself causes a line broadening. A few examples will illustrate the case we have in mind.

(a) We consider the Mössbauer experiment of iron (^{57}Fe) dissolved in a liquid mixture of phosphoric acid and water ($H_3PO_4 + H_2O$).[2] As the temperature of the system is raised through its glass transition, the nucleus jumps from one position to another to find itself in differently oriented electric field gradients produced by its surroundings. So the nuclear quadrupolar interaction changes its form each time the nucleus changes position. If the Hamiltonian is diagonalized at one instant of time each jump of the nucleus changes the quantization axis and the new Hamiltonians can induce transitions between the energy levels of the diagonal Hamiltonian.

(b) A Mössbauer experiment is performed in an antiferromagnet where in the simplest case, the system may be described by two sublattices with oppositely directed magnetization vectors. As the nucleus jumps from one lattice site to another, the effective magnetic field (which interacts with the magnetic dipole moment of the nucleus) reverses its direction. Although the two possible forms of the Hamiltonian commute in this case, the change in direction of the effective field nevertheless introduces relaxation effects. Of course, the magnetic order in the sample is to be preserved even at temperatures when diffusion starts to take place. Such antiferromagnets with high transition temperatures are available in nature.[6] A good candidate seems to be the binary alloy MnNi which has a Néel temperature of 1140 °K.

(c) Some ferromagnetic alloys, e.g., iron and cobalt, have high Curie temperatures.[7] In such a system, the magnetization vector, though pointing in the same direction, has a magnitude at the iron site different from that at the cobalt site.[8] If radioactive Mössbauer nuclei are imbedded in such a system and the nuclei are made to diffuse from one site to another, they will have different Zeeman interactions at different sites again giving rise to relaxation effects.

In all these examples above, what goes on physically is this. Each time the nucleus makes a jump, the phase of the emitted or absorbed γ ray changes. At the same time, however, the nucleus may find itself in a different energy state, so the frequency of the radiation also changes. While the existing theoretical calculations of relaxation effects deal with frequency modulation alone (with an implicit assumption of no phase change, i.e., a stationary nucleus), we are considering here a circumstance where both phase and frequency modulations are involved simultaneously.

An outline of the paper is as follows. In Sec. II, we write the expression for the Mössbauer emission line shape in terms of a correlation function. The effect of the surroundings of the nucleus in evaluating this correlation function is treated entirely classically in a stochastic-theory model. The assumed nature of motion of the nucleus which enables us to separate the diffusive and vibrational parts of the motion, is indicated in Sec. III. In Sec. IV we present the model and its mathematical solution. The utility of the model is exemplified in Sec. V by considering an experimental case.[2] We plot our results for the line shape as a function of two parameters: (i) the rate of diffusion of the nucleus, and (ii) a factor which measures the probability that the nucleus jumps to a different position. Finally, Sec. VI contains a brief summary of our work.

II. EMISSION PROBABILITY

We want to calculate the probability of emission of a γ ray of wave vector $\vec{k}$ by a single nucleus which is a part of a many-body system consisting of the solid or liquid in which the nucleus is embedded. As shown by Singwi and Sjölander,[4a] the Hamiltonian H' which governs the emission or absorption of a γ ray and which represents the interaction between the radiation field and the nucleus can be written

$$H' = A e^{i\vec{k}\cdot\vec{R}} , \tag{1}$$

where $\vec{R}$ is the coordinate of the center of mass of the nucleus and A is an operator which acts only on the internal quantum mechanical state (e.g., the spin angular momentum state) of the nucleus. The matrix elements of A which determine the intensity and the polarization of the emitted or absorbed radiation, can be written in terms of a Clebsch-Gordan coefficient. The operator $\vec{R}$, on the other hand, acts on the state which determines the collective motions of the centers of masses.

The probability of emission of a γ ray of frequency ω may be written as the real part of the Laplace transform of a correlation function

$$\Phi(p, \vec{k}) = \mathrm{Re} \int_0^\infty dt\, e^{-pt}\, \mathrm{Tr}(\rho A e^{i\vec{k}\cdot\vec{R}} e^{i\mathcal{H}t} A^\dagger e^{-i\vec{k}\cdot\vec{R}} e^{-i\mathcal{H}t}) , \tag{2}$$

where $p = i\omega + \frac{1}{2}\Gamma$, Γ being the natural linewidth of the excited level, $\mathcal{H}$ is the Hamiltonian for the entire many-body system containing the nucleus plus its surroundings, ρ is the equilibrium density matrix for the entire system governed by the Hamiltonian $\mathcal{H}$, and the trace is calculated over the many-body states of $\mathcal{H}$. We would like to write (2) as

$$\Phi(p, \vec{k}) = \mathrm{Re} \int_0^\infty dt\, e^{-pt} \int d\vec{r}\, e^{i\vec{k}\cdot\vec{r}}\, \Phi(\vec{r}, t) , \tag{3}$$

where, by definition,

$$\Phi(\vec{r}, t) = \frac{1}{(2\pi)^3} \int d\vec{k}'\, e^{-i\vec{k}'\cdot\vec{r}} \times \mathrm{Tr}(\rho A e^{i\vec{k}'\cdot\vec{R}} e^{i\mathcal{H}t} A^\dagger e^{-i\vec{k}'\cdot\vec{R}} e^{-i\mathcal{H}t}). \tag{4}$$

In the case considered by Singwi and Sjölander and others,[4] where they are concerned only with the diffusive motion of the nucleus, the internal state of the nucleus is assumed to be not influenced by the heat bath, so $\mathcal{H}$ and A commute. In that case,

$$\Phi(\vec{r}, t) = \mathrm{Tr}_n(\rho_n A A^\dagger)\, G_s(\vec{r}, t) , \tag{5}$$

where

$$G_s(\vec{r}, t) = \frac{1}{(2\pi)^3} \int d\vec{k}'\, e^{-i\vec{k}'\cdot\vec{r}}\, \mathrm{Tr}_b(\rho_b e^{i\vec{k}'\cdot\vec{R}} e^{-i\vec{k}'\cdot\vec{R}(t)}) , \tag{6}$$

ρ_b is the density matrix for the heat bath, ρ_n is the density matrix for the internal states of the nucleus, $\mathrm{Tr}_b(\cdots)$ and $\mathrm{Tr}_n(\cdots)$ represent trace operations over states of the heat bath and the nuclear system respectively, and

$$\vec{R}(t) = e^{i\mathcal{H}t}\, \vec{R}\, e^{-i\mathcal{H}t} . \tag{7}$$

G_s is the Van Hove correlation function.[9]

The subscript s in $G_s(\vec{r}, t)$ [Eq. (6)] stands for "self" which means that G_s measures the correlation between the positions of the same nucleus at two different times.

On the other hand, in the existing calculations of relaxation effects, it is assumed that the nucleus does not move at all.[1] So from (2),

$$\Phi(p) = \mathrm{Re} \int_0^\infty dt\, e^{-pt}\, \mathrm{Tr}[\rho A A^\dagger(t)] , \tag{8}$$

where $A^\dagger(t)$ is defined in a manner similar to (7). In this case the time development of $A^\dagger$ is determined by magnetic hyperfine or electric quadrupole interaction modulated by other extranuclear interactions.

In this paper we want to consider the general case represented by Eqs. (2)–(4), where both $\vec{R}$ and A are influenced by the Hamiltonian. However, $\vec{R}$ always commutes with A.

III. NATURE OF DIFFUSIVE MOTION

In calculating $\Phi(\vec{r}, t)$ in (3), we consider diffusive motion in solids and liquids. Diffusion of atoms in solids usually takes place in the form of large independent jumps to vacant sites. An atom in a solid performs a large number of oscillations at one site before it jumps to a neighboring site. Accordingly, we have

$$\tau \gg (\bar{\omega})^{-1} , \tag{9}$$

and

$$\tau \gg \tau' , \tag{10}$$

where τ is the average time between successive jumps, $(\bar{\omega})^{-1}$ is the average time of oscillation of the atom at a site or the inverse of the Debye frequency, τ' is the average time of transit during a jump. Therefore, we assume that in a solid, the oscillatory and diffusive motions are completely uncorrelated and that the diffusion takes place very rapidly [cf. condition (10)] so that the oscillatory motion has gone on for the whole time interval t.[10] Thus we write

$$\gamma_s(\vec{k}, t) = \int d\vec{r}\, e^{i\vec{k}\cdot\vec{r}} G_s(\vec{r}, t) = \gamma_s^D(\vec{k}, t)\gamma_s^V(\vec{k}, t) , \tag{11}$$

where γ^D describes the diffusive and γ^V the vibrational motion.

In liquids also, it was thought at one time that diffusion of atoms is solidlike. Experimental neutron-scattering results in liquids like water[11] and lead[12] were interpreted on the basis of this picture of a jump diffusion model. However, molecular dynamics studies[13] do not support this quasicrystalline model for diffusion of atoms in liquids. While it is reasonable to assume that in liquids, diffusion occurs in the form of very short jumps, i.e., a quasicontinuous motion as indicated by the molecular-dynamics studies, it is nevertheless possible in highly viscous liquids at low temperature that the atom moves by a very short step only after a measurable stay at one site. We emphasize that the time τ in (9) which measures the duration of stay at a site could, in a highly viscous liquid at low temperatures, be still larger than the characteristic inverse frequency $(\bar{\omega})^{-1}$ of oscillation [cf. assumption (9)]. Assumption (10), on the other hand, is actually better in liquids when the jump lengths are shorter. The arguments above mean that in liquids, even though diffusion may take place by very short jumps, under suitable circumstances, a separation of the self-correlation function in diffusive and vibratory parts, is meaningful. In this paper, we shall be dealing only with systems for which (11) is approximately satisfied. The vibrational part $\gamma_s^V(\vec{k}, t)$ in (11) has been discussed at length by Van Hove,[9] Vineyard,[14] and others. In this paper, we shall not concern ourselves with the calculation of $\gamma_s^V(\vec{k}, t)$ and therefore set it equal to unity. This means that for our purpose the $\vec{r}$ dependence in $\Phi(\vec{r}, t)$ in (3) arises solely from diffusive motion. Furthermore, we shall treat the diffusive motion classically so that we can interpret $G_s(\vec{r}, t)$ as the probability of finding the nucleus at the position $\vec{r}$ at time t given that it was at the origin at $t=0$.[9] In a Mössbauer experiment in which the γ ray energy width is much less than thermal energies ($\Gamma \ll KT$, K is the Boltzmann constant) this completely classical interpretation of $G_s(\vec{r}, t)$ is sufficient.[15] We must emphasize, however, that the problem of calculating the $\vec{r}$ dependence in $\Phi(\vec{r}, t)$ in (3), determined by the diffusive motion cannot be disentangled from the quantum-mechanical problem of evaluating the time development of the operator $A^\dagger$. As we saw in the examples discussed in Sec. I, each jump throws the nucleus into a different quantum-mechanical state. So the effect of each single jump on the position and the internal quantum state of the nucleus has to be calculated simultaneously.

IV. MATHEMATICAL MODEL AND ITS SOLUTION

We assume that the effect of the heat bath is to subject the nucleus to sudden pulses at random instants of time. Each such pulse causes the nucleus to jump instantaneously [cf. assumption (10)] to a new site. So each pulse causes an instantaneous change in phase of the emitted γ ray. At the same time, the jump takes the nucleus to a new environment where it "sees" a different Hamiltonian. In between pulses, the nucleus is assumed unperturbed. The instants t_i at which the pulses occur are assumed random with a Poisson distribution. The physical idea we use here is borrowed from a stochastic theory model considered by Clauser and Blume[16] to study relaxation effects in line-shape problems.

In this stochastic model, the statistical average over the degrees of freedom of the heat bath in (4) is replaced by an average over the stochastic properties of the system Hamiltonian.[16,17] So the line shape, from Eqs. (3) and (4), is given by

$$\Phi(p, \vec{k}) = \mathrm{Re}\int_0^\infty dt\, e^{-pt} \int d\vec{r}\, e^{i\vec{k}\cdot\vec{r}}\Phi(\vec{r}, t) , \tag{12}$$

$$\Phi(\vec{r}, t) = \mathrm{Tr}_n[\rho_n A (U(\vec{r}, t))_{\mathrm{av}} A^\dagger] , \tag{13}$$

where $U(\vec{r}, t)$ is a quantum-mechanical super operator for the nucleus which determines both the time and the position developments of the nucleus under the influence of the heat bath. $(\ )_{\mathrm{av}}$ denotes a stochastic average over the type of pulses and the instants t_i and positions $\vec{r}_i$ at which they occur. The remaining trace operation in (18) is now performed over only the internal degrees of freedom of the nucleus.

The meaning of $U(\vec{r}, t)$ becomes clear in the two limiting cases we have been discussing. In the purely diffusive case, the internal degrees of freedom of the nucleus are assumed not influenced by the lattice.[4] So $U(\vec{r}, t)$ simply becomes the Van Hove self-diffusion correlation function. On the other hand, in the pure relaxation case, there is no $\vec{r}$ dependence in (13) and

$$(U(\vec{r}, t))_{\rm av} \equiv (U(\vec{r}=0, t))_{\rm av} = \left[\exp\left(i\int_0^t \mathcal{H}^{\times}(t')\,dt'\right)\right]_{\rm av} \quad , \tag{14}$$

a time-ordered product where $\mathcal{H}^{\times}(t)$ is the Liouville operator associated with the interaction Hamiltonian $\mathcal{H}(t)$.[18] The Liouville operator is defined by

$$[\mathcal{H}, A] = \mathcal{H}^{\times} A \quad . \tag{15}$$

Equation (15) allows us to write

$$\exp\left(i\int_0^t \mathcal{H}(t')\,dt'\right) A \exp\left(-i\int_0^t \mathcal{H}(t')\,dt'\right) = \left[\exp\left(i\int_0^t \mathcal{H}^{\times}(t')\,dt'\right) A\right] \quad , \tag{16}$$

with suitable time ordering.[17] Thus $\mathcal{H}^{\times}(t)$ determines the time development of operator A in the interaction representation.

In the general case when the heat bath or the lattice affects both the internal state and the position of the nucleus, we cannot give such a simple physical interpretation to $U(\vec{r}, t)$. However, its meaning becomes apparent when we write down the mathematical expression for it [cf. Eq. (20)]. In our model each pulse causes the nucleus to jump to a new stochastic state (labeled by indices $a, b, c, \ldots$) with a different Hamiltonian. So we would like to picture $U(\vec{r}, t)$ as a matrix $\mathcal{U}(\vec{r}, t)$ in the stochastic variable space (its dimension is $n\times n$ if n is the number of different forms of the Hamiltonian at different sites).[17] We may write the matrix $\mathcal{U}(\vec{r}, t)$ as

$$\begin{aligned}\mathcal{U}(\vec{r}, t) &\equiv \mathcal{U}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r};\ t_1, t_2, \ldots, t)\\ &= e^{i\mathcal{H}_0^{\times}t_1} g(0, \vec{r})\mathcal{T} e^{i\mathcal{H}_0^{\times}(t_1-t_2)} g(\vec{r}_1, \vec{r}_2)\mathcal{T} e^{i\mathcal{H}_0^{\times}(t_3-t_2)}\\ &\quad \times \cdots g(\vec{r}_{s-1}, \vec{r}_s=\vec{r})\mathcal{T} e^{i\mathcal{H}_0^{\times}(t-t_s)} \quad ,\end{aligned} \tag{17}$$

where

$$\mathcal{H}_0^{\times} = \sum_{j=1}^{n} V_j^{\times} F_j \quad . \tag{18}$$

$V_j^{\times}$ is a quantum-mechanical Liouville operator associated with the jth form of the Hamiltonian V_j, F_j is a stochastic matrix[17] defined by

$$(a|F_j|b) = \delta_{aj}\delta_{ab} \quad , \tag{19}$$

the matrix $(a|\mathcal{T}|b)$ is the probability that a jump takes the nucleus from a stochastic state a to another b and $g(\vec{r}_1, \vec{r}_2)$ is the probability that a jump takes the nucleus from $\vec{r}_1$ to $\vec{r}_2$.[19] The stochastic process is assumed to be stationary so that $\mathcal{T}$ and g do not depend on the time at which the jump occurs.

From (17)–(19), the matrix element of $\mathcal{U}(\vec{r}, t)$ in the stochastic space is given by

$$\begin{aligned}(a|\mathcal{U}(\vec{r}, t)|b) = \sum_{cd\cdots} & e^{iV_a^{\times}t_1} g(\vec{r}_1)\mathcal{T}_{ac}\\ &\times e^{iV_c^{\times}(t_2-t_1)} g(\vec{r}_1, \vec{r}_2)\mathcal{T}_{cd}\\ &\times e^{iV_d^{\times}(t_3-t_2)} \cdots g(\vec{r}_{s-1}, \vec{r}_s=\vec{r})\\ &\times \mathcal{T}_{db} e^{iV_b^{\times}(t-t_s)} \quad .\end{aligned} \tag{20}$$

The meaning of (20) is this. At $t=0$, the nucleus starts at the origin $\vec{r}=0$ where it "sees" a Hamiltonian V_a. Its quantum-mechanical state develops in time to t_1 given by the appropriate time-development super operator $e^{iV_a^{\times}t_1}$. At t_1, a pulse hits the nucleus which has a probability $g(\vec{r}=0, \vec{r}_1)$ of taking it instantaneously to the position $\vec{r}_1$ and a probability $\mathcal{T}_{ac}$ of throwing it simultaneously into a stochastic state c governed by a Hamiltonian V_c. Its quantum-mechanical state then develops under V_c until a time t_2 at which point another pulse makes it jump to $\vec{r}_2$ into a stochastic state d and so on. Of course, we have to consider all possible intermediate stochastic states, so we sum over the stochastic variables $c, d, \cdots$.

The final average we seek in (13) is obtained by summing over the final stochastic states b, averaging over the initial states a and averaging over the type and location (both in space and time) of the pulses. That is

$$\begin{aligned}(U(\vec{r}, t))_{\rm av} = \sum_{s=0}^{\infty} P_s(t)\int_0^t dt_s \int_0^{t_s} dt_{s-1} \cdots \int_0^{t_2} dt_1 \int d\vec{r}_{s-1}\int d\vec{r}_{s-2} \cdots \int d\vec{r}_1\, W_s(t_1, \ldots, t_s, t)\\ \times \sum_{ab} p_a(a|\mathcal{U}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_s=\vec{r}; t_1, t_2, \ldots, t)|b) \ ,\end{aligned} \tag{21}$$

where p_a is the *a priori* probability of the occurrence of the initial stochastic state a and $P_s(t)$ is the probability that exactly s pulses occur in time t. For random occurrence of the pulses, this is given by the Poisson distribution[16]

$$P_s(t) = [(\lambda t)^s/s!]\,e^{-\lambda t} \ , \tag{22}$$

where $\lambda^{-1}=\tau$ is the mean time between pulses; τ is the mean time between two successive jumps of the nucleus. Also $W_s(t_1, \ldots, t_s; t)\, dt_1, \ldots, dt_s$ is the probability that, given that s pulses occur in time t, these occur at t_1 in $dt_1, \ldots, t_s$ in dt_s, respectively. Since the points are randomly distributed,

$$W_s = s!/t^s . \tag{23}$$

We also assume translational invariance

$$g(\vec{r}_1, \vec{r}_2) = g(\vec{r}_2 - \vec{r}_1) . \tag{24}$$

Combining (21)–(24), we have

$$\begin{aligned}(U(\vec{r}, t))_{\mathrm{av}} = \sum_{s=0}^{\infty} \int_0^t dt_s \cdots \int_0^{t_2} dt_1 \int d\vec{r}_{s-1} \cdots \int d\vec{r}_1 \sum_{ab} p_a (a|\, e^{-(\lambda - i\mathcal{H}_0^{\times})t_1} [g(\vec{r}_1)\lambda \mathcal{T}] \\ \times e^{-(\lambda - i\mathcal{H}_0^{\times})(t_2 - t_1)} [g(\vec{r}_2 - \vec{r}_1)\lambda\mathcal{T}] \cdots [g(\vec{r} - \vec{r}_{s-1})\lambda\mathcal{T}]\, e^{-(\lambda - i\mathcal{H}_0^{\times})(t - t_s)} |\, b) .\end{aligned} \tag{25}$$

Using the convolution theorem for Laplace and Fourier transforms, we have

$$\begin{aligned}\int_0^{\infty} dt\, e^{-pt} \int d\vec{r}\, e^{i\vec{k}\cdot\vec{r}} (U(\vec{r}, t))_{\mathrm{av}} &= \sum_{ab} p_a \left(a \left| \left\{ \sum_{s=0}^{\infty} \frac{1}{p + \lambda - i\mathcal{H}_0^{\times}} [g(\vec{k})\lambda\mathcal{T}] \frac{1}{p + \lambda - i\mathcal{H}_0^{\times}} [g(\vec{k})\lambda\mathcal{T}] \right.\right.\right. \\ &\quad \left.\left.\left. \times \cdots [g(\vec{k})\lambda\mathcal{T}] \frac{1}{p + \lambda - i\mathcal{H}_0^{\times}} \right\} \right| b \right) = \sum_{ab} p_a \left(a \left| \left\{ \sum_{s=0}^{\infty} \frac{1}{p+\lambda - i\mathcal{H}_0^{\times}} \left(\lambda g(\vec{k}) \mathcal{T} \frac{1}{p + \lambda - i\mathcal{H}_0^{\times}} \right)^s \right\} \right| b \right) \\ &= \sum_{ab} p_a \left(a \left| \frac{1}{p + \lambda - i\mathcal{H}_0^{\times} - \lambda g(\vec{k})\mathcal{T}} \right| b \right) ,\end{aligned} \tag{26}$$

where

$$g(\vec{k}) = \int d\vec{r}\, e^{i\vec{k}\cdot\vec{r}} g(\vec{r}) . \tag{27}$$

Substituting in (12) the final solution to the line-shape problem is given by

$$\Phi(p, \vec{k}) = \mathrm{Re}\,\mathrm{Tr}_n \left(\rho_n A \sum_{ab} p_a (a|\, [p + \lambda - i\mathcal{H}_0^{\times} - \lambda g(\vec{k})\mathcal{T}]^{-1} |\, b) A^{\dagger} \right) . \tag{28}$$

The solution as given by (28) involves the inversion of a matrix which is labeled by both quantum-mechanical and stochastic indices. For example, in the case of a Mössbauer emission from an excited state of spin I_e to a ground state of spin I_g, the dimension of the matrix to be inverted is $(2I_e + 1) \times (2I_g + 1)n$, where n is the number of different forms of the Hamiltonian.[17] This can be handled on a computer or in some cases, analytically. Let us discuss the result (28) in two limiting cases.

(i) If the nucleus remains stationary at the origin, $g(\vec{r}) = \delta(\vec{r})$. Then from (27), $g(\vec{k}) = 1$. In that case, Eq. (28) reduces to the result obtained by Blume for the stochastic theory solution of Mössbauer line shape in presence of extranuclear perturbations.[17]

(ii) If the quantum-mechanical state of the system does not change with each nuclear jump, i.e., the lattice has no effect on the internal degrees of freedom of the nucleus, we may put $V_j^{\times} = \omega_0$, the frequency of the emitted γ ray ($\hbar = 1$). So from (18) and (19),

$$\mathcal{H}_0^{\times} = \omega_0 \sum_{j=1}^{n} F_j = \omega_0 . \tag{29}$$

From (28) we have

$$\Phi(p, \vec{k}) = \mathrm{Re}\left(C \sum_{ab} p_a (a|\, [p + \lambda - i\omega_0 - \lambda g(\vec{k})\mathcal{T}]^{-1} |\, b) \right) , \tag{30}$$

where $C = \mathrm{Tr}_n(\rho_n A A^{\dagger})$ is a constant;

$$\Phi(p, \vec{k}) = \mathrm{Re}\left\{ \frac{C}{p + \lambda - i\omega_0} \times \sum_{s=0}^{\infty} \left[\left(\frac{\lambda g(\vec{k})}{p + \lambda - i\omega_0} \right)^s \sum_{ab} p_a (a|\, \mathcal{T}^s |\, b) \right] \right\} .$$

Now,

$$\sum_{ab} p_a (a|\, \mathcal{T}^s |\, b) = \sum_{abcd\cdots} p_a (a|\, \mathcal{T} \,|\, c)(c\,|\, \mathcal{T} \,|\, d) \cdots (e\,|\, \mathcal{T} \,|\, b) = \sum_a p_a = 1 ,$$

since $\sum_b (d|\,\mathcal{T}\,|\,b)$ = total probability of transition from the stochastic state d which is equal to one. Therefore, in this case

$$\Phi(p, \vec{k}) = \mathrm{Re}\left(\frac{1}{p + \lambda[1 - g(\vec{k})] - i\omega_0} \right) . \tag{31}$$

Recalling that $p = i\omega + \frac{1}{2}\Gamma$ (Γ is the natural linewidth of the excited nuclear state), Eq. (31) predicts a Mössbauer line centered around ω_0 and broadened by an amount $2\lambda[1 - g(\vec{k})]$, where λ^{-1} is the mean time between two successive nuclear jumps. This is the so called diffusion broadening which was derived by Singwi and Sjölander, among others.[4]

The solution in (28) requires knowledge of the transition matrix $\mathcal{T}$. In Sec. V we consider a particular form for $\mathcal{T}$ which allows us to give a simple analytical expression for the line shape.

V. EXAMPLE: RANDOMLY ORIENTED ELECTRIC FIELD GRADIENT

A. Diffusion in phosphoric acid

As an illustration of the applicability of our theory we consider the Mössbauer experiment of Ruby *et al.*[2,30] The system studied is a solution of phosphoric acid and water which exhibits a glass transition. The probe is a Mössbauer nucleus ^{57}Fe which emits a 14.4-keV γ ray. At low temperatures when the system is in the ordered state, the nucleus is surrounded by six oxygen atoms. Some of these oxygen atoms belong to water molecules, some to phosphate molecules and are not chemically equivalent as far as their electric charges are concerned. This charge asymmetry plus the geometrical location of the oxygen atoms give rise to a nearly axial electric field gradient at the site of the nucleus. This interacts with the quadrupole moment of the nucleus yielding a spectrum which at low temperatures, is a quadrupole doublet corresponding to the fact that ^{57}Fe has a spin $\frac{3}{2}$ in the excited state and a spin $\frac{1}{2}$ in the ground state. As the temperature of the system is raised towards its glass transition, the iron nucleus starts to diffuse. But as it moves to a new position, a slight rearrangement of the surrounding oxygen atoms is sufficient to cause the field gradient to change its direction arbitrarily.[20]

As the rate of diffusion increases, the two lines of the quadrupole pattern are expected to broaden due to (i) nuclear motion and (ii) relaxation mechanism arising from a change in orientation of the electric field gradient.[21] The second mechanism also gives rise to a shift of the lines towards the center of the pattern. Finally, when the rate is so large that the nucleus "sees" a zero time-averaged field gradient we expect to see a single line.

B. Classical analogy

This problem has an interesting classical analogy. The Mössbauer emission of a γ ray from a nucleus undergoing jump diffusion can be compared with the transmission of a signal from an oscillator subject to random collisions of exceedingly short duration. Suppose the transmitter is tuned to two frequencies $\omega_0 \pm \Delta\omega$ ($\Delta\omega$ corresponds to the quadrupole splitting in the excited state of the nucleus and ω_0 to the unperturbed energy of the γ ray). At each impact, the transmitter jumps to a new position with a sudden change in phase. At the same time, the collision switches the frequency from one value to the other. Such a problem was considered by Van Vleck[22] who treated two special cases: (i) complete persistence in position and velocity of the oscillator at each collision. This in our notation means $g(\vec{k})=1$; (ii) no persistence at all, i.e., $g(\vec{k})=0$. In our problem we would like to determine the line shape for all possible values of $g(\vec{k})$ between 0 and 1, depending on the nature of jump.

C. Theoretical analysis

Coming back to the theoretical analysis of the experiment in phosphoric acid, since the electric field gradients at different sites are randomly oriented, the transition probabilities to all stochastic states are equal. Accordingly,

$$(a|\mathcal{T}|b)=1/n\ , \tag{32}$$

where n is the number of possible orientations of the field gradient. The *a priori* probabilities p_a of Eq. (21) are all equal in this case:

$$p_a=1/n\ . \tag{33}$$

The form of the transition matrix in (32) which is used in the so called strong collision model enables us to eliminate the stochastic indices from the expression (28) of the line shape.[23] Before we do this, let us make use of another simple feature of the problem, viz., the fact that ^{57}Fe has a zero quadrupole interaction in the ground state (spin $=\frac{1}{2}$). This means that if we write out the trace[17] in (28) we get

$$\begin{aligned}\Phi(p,\vec{k}) = \operatorname{Re}\frac{1}{2I_e+1} & \times\sum_{M_eM_e'}\sum_{m_gm_g'}\langle M_e|A|m_g\rangle\langle m_g'|A^\dagger|M_e'\rangle\delta_{m_gm_g'} \\ & \times\sum_{ab}p_a(a|\{\langle M_e|[p+\lambda-i\mathcal{H}_0 \\ & -\lambda g(\vec{k})\mathcal{T}]^{-1}|M_e'\rangle\}|b)\ ,\end{aligned} \tag{34}$$

where $\mathcal{H}_0$ is now an ordinary operator describing the interaction in the excited state of the nucleus. In (34) we have assumed that the temperature is high enough, so the nuclear excited levels are equally populated, i.e., $\rho_n=1/(2I_e+1)$, I_e $(=\frac{3}{2})$ being the spin of the nucleus in the excited state. From (18), $\mathcal{H}_0$ is given by

$$\mathcal{H}_0=\sum_{j=1}^{n}V_jF_j\ ,$$

where in this case

$$V_j=\omega_0+Q[3(I_e^j)^2-I_e(I_e+1)]\ , \tag{35}$$

where ω_0 is the frequency of the emitted γ ray (=14.4 keV for ^{57}Fe); Q is the quadrupole moment of the nucleus, and I_e^j is the spin of the nucleus in the excited state along the jth direction of the field gradient.

As shown in Ref. 23, the forms of $\mathcal{T}$ and p_a given in (32) and (33) allow us to write the line shape in (34) as

$$\Phi(p,\vec{k}) = \mathrm{Re}\frac{1}{2I_e+1}\sum_{\substack{M_e M_e'\\ m_g}} \langle M_e|A|m_g\rangle\langle m_g|A^\dagger|M_e'\rangle \times\langle M_e|\frac{(U^0(p+\lambda))_{\mathrm{av}}}{1-\lambda g(\vec{k})(U^0(p+\lambda))_{\mathrm{av}}}|M_e'\rangle, \qquad (36)$$

where the quantum mechanical operator $(U^0(p+\lambda))_{\mathrm{av}}$ is given by

$$(U^0(p+\lambda))_{\mathrm{av}} = \frac{1}{n}\sum_{j=1}^{n}\frac{1}{p+\lambda-iV_j}, \qquad (37)$$

V_j being given by (35). In the limit when the field gradients are distributed isotropically in space, we may write

$$(U^0(p+\lambda))_{\mathrm{av}} = \frac{1}{4\pi}\int\frac{d\Omega_j}{p+\lambda-iV_j}, \qquad (38)$$

where $d\Omega_j$ is the elementary solid angle in the jth direction.[23] Let us now determine the matrix elements of $(U^0(p+\lambda))_{\mathrm{av}}$:

$$\langle M_e|(U^0(p+\lambda))_{\mathrm{av}}|M_e'\rangle = \frac{1}{4\pi}\int d\Omega_j\int_0^\infty dt\, e^{-(p+\lambda)t}\langle M_e|e^{iV_j t}|M_e'\rangle, \qquad (39)$$

from (38), where the z axis is assumed to be the axis of quantization so that $|M_e\rangle$ is an eigenstate of I_e^z. We may write

$$D^{(I_e)}(\Omega_j)\,e^{iV_j t}[D^{(I_e)}(\Omega_j)]^{-1} = e^{iV_z t}, \qquad (40)$$

where $D^{(I_e)}(\Omega_j)$ is a rotation operator[24] in the angular momentum space of I_e which transforms the jth direction to the z direction, and

$$V_z = \omega_0 + Q[3(I_e^z)^2 - I_e(I_e+1)], \qquad (41)$$

from (35).

Substituting (40) into (39),

$$\langle M_e|(U^0(p+\lambda))_{\mathrm{av}}|M_e'\rangle = \frac{1}{4\pi}\sum_{M''}\frac{1}{p+\lambda-iV_{M_e''}} \times\int d\Omega_j\langle M_e|D^{(I_e)}(\Omega_j)|M_e''\rangle \times\langle M_e''|D^{(I_e)^{-1}}(\Omega_j)|M_e'\rangle,$$

where, from (41),

$$V_{M_e''} = \omega_0 + Q[3(M_e'')^2 - I_e(I_e+1)]. \qquad (42)$$

Using the orthogonality property[24] of the D matrices

$$\frac{1}{4\pi}\int d\Omega\langle M_e|D(\Omega)|M_e''\rangle\langle M_e''|D^{-1}(\Omega)|M_e'\rangle = \frac{\delta_{M_e M_e'}}{2I_e+1},$$

we obtain

$$\langle M_e|(U^0(p+\lambda))_{\mathrm{av}}|M_e'\rangle = \frac{\delta_{M_e M_e'}}{2I_e+1}\sum_{M_e''}\frac{1}{p+\lambda-iV_{M_e''}}. \qquad (43)$$

Thus, $(U^0(p+\lambda))_{\mathrm{av}}$ is diagonal in the angular momentum representation of I_e^z which we obviously expect for an isotropic operator.

Using (42) and (43) and the fact that the $I_e=\frac{3}{2}$, we have

$$\langle M_e|(U^0(p+\lambda))_{\mathrm{av}}|M_e'\rangle = \delta_{M_e M_e'}\frac{p+\lambda-i\omega_0}{(p+\lambda-i\omega_0)^2+9Q^2}. \qquad (44)$$

Substituting (44) into (36), the final expression for the Mössbauer-emission line shape is obtained as

$$\Phi(p,\vec{k}) = \mathrm{Re}\left[\frac{1}{4}\sum_{M_e m_g}|\langle M_e|A|m_g\rangle|^2 \times\left(p-i\omega_0+\lambda[1-g(\vec{k})]+\frac{9Q^2}{p+\lambda-i\omega_0}\right)^{-1}\right] = \mathrm{Re}\left[\left(p-i\omega_0+\lambda[1-g(\vec{k})]+\frac{9Q^2}{p+\lambda-i\omega_0}\right)^{-1}\right]. \qquad (45)$$

Thus, we find that the simple form of the transition matrix [cf. Eq. (32)] and the assumption of isotropy [cf. Eq. (38)] enable us to overcome the problem of matrix inversion in (28) and give a simple closed form expression for the line shape. The additional symmetry of zero quadrupole splitting in the ground state of ^{57}Fe nucleus, though a simplifying feature, is not a necessary condition[23] for obtaining (45). Let us consider the line shape in three special cases.

Case I: $Q=0$.

$$\Phi(p,\vec{k}) = \mathrm{Re}\left(\frac{\text{constant}}{p-i\omega_0+\lambda[1-g(\vec{k})]}\right), \qquad (46)$$

which yields a Lorentzian line centered around ω_0 with a width $2\lambda[1-g(\vec{k})]$. This is the result of Singwi and Sjölander.[4]

Case II: $g(\vec{k})=1$. *Stationary nucleus* in a fluctuating environment of randomly varying electric field gradients.[21]

$$\Phi(p) = \mathrm{Re}\left(\frac{1}{p-i\omega_0+9Q^2/(p+\lambda-i\omega_0)}\right), \qquad (47)$$

the expression (44) obtained in Ref. 23.

Case III: $g(\vec{k})=0$. *No phase memory at all.*

$$\Phi(p) = \mathrm{Re}\left(\frac{\frac{1}{2}}{p+\lambda-i\omega_0+i3Q}+\frac{\frac{1}{2}}{p+\lambda-i\omega_0-i3Q}\right). \qquad (48)$$

Equation (48) predicts a superposition of two lines centered around (ω_0-3Q) and (ω_0+3Q), each broadened by an amount $\lambda+\frac{1}{2}\Gamma$ $(p=i\omega+\frac{1}{2}\Gamma)$. This can now be directly compared with Eq. (17) of Van Vleck's classical oscillator model solution.[22]

Equation (48) leads to an interesting result that as the jump rate λ increases, the two lines start to broaden separately to reach a point when their su-

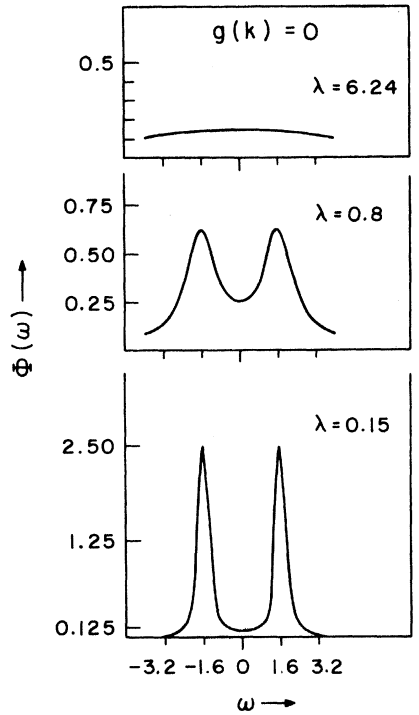

FIG. 1. Mössbauer line shape for different values of the rate of diffusion λ in the case $g(k) = 0$ which corresponds to a completely random phase situation.

perposition is a single broad line (cf. Fig. 1). They do not, however, exhibit a shift toward the center of the pattern to form a single line and a subsequent motional narrowing of that line as is characteristic in a pure relaxation spectrum involving two frequencies $\omega_0 \pm \Delta\omega$. In our case, this has the following physical interpretation.

Suppose the Mössbauer nucleus starts from a position where the field gradient is in the z direction. The z axis therefore is the appropriate axis of quantization for the quadrupolar interaction at $t = 0$. Then at time t_1, the nucleus jumps to a new position where it finds the field gradient in the x direction, say. In a normal situation, the new Hamiltonian will be off-diagonal with respect to the previous axis of quantization and therefore will induce relaxation effects. However, $g(\vec{k}) = 0$ now which means that the nucleus has absolutely no memory of its previous axis of quantization. So it adjusts itself to the x axis as its new axis of quantization with no "hangover."[25] The new quadrupolar interaction [cf. Eq. (35)]

$$V_x = \omega_0 + Q[(3I_e^x)^2 - I_e(I_e + 1)]$$

obviously has the same two eigenvalues ($\omega_0 \pm 3Q$). Therefore the spectrum in this case is simply an incoherent sum of two Lorentzians as given in (48). The same result would also be obtained in the case when the field gradients are pointed in the same direction at all sites and the nucleus jumps between them.

The line shape for an arbitrary value of $g(\vec{k})$ between 0 and 1 can be expressed from (45) as

$$\Phi(p, \vec{k}) \sim \mathrm{Re}\left(\frac{1 - \lambda g(\vec{k})\{[\lambda g(\vec{k})]^2 - 36Q^2\}^{-1/2}}{p - i\omega_0 + \lambda[1 - \frac{1}{2}g(\vec{k})] + \frac{1}{2}\{[\lambda g(\vec{k})]^2 - 36Q^2\}^{1/2}} + \frac{1 + \lambda g(\vec{k})\{[\lambda g(\vec{k})]^2 - 36Q^2\}^{-1/2}}{p - i\omega_0 + \lambda[1 - \frac{1}{2}g(\vec{k})] - \frac{1}{2}\{[\lambda g(\vec{k})]^2 - 36Q^2\}^{1/2}}\right). \tag{49}$$

For $\lambda g(\vec{k}) < 6Q$ [trivially satisfied for $g(\vec{k}) = 0$], the radical is imaginary and a splitting into two lines is found, while for $\lambda g(\vec{k}) > 6Q$, the radical is real and contributes to the width. If for some $g(\vec{k})$, $\lambda g(\vec{k}) \gg 6Q$ such that $36Q^2/[\lambda g(\vec{k})]^2 \approx 0$, Eq. (49) yields

$$\Phi(p, \vec{k}) \approx \mathrm{Re}\left(\frac{\text{constant}}{p - i\omega_0 + \lambda[1 - g(\vec{k})]}\right), \tag{50}$$

a single line around ω_0 of width $2\lambda[1 - g(\vec{k})]$ which, for a large λ could be comparable to or even bigger than the natural line width Γ even if $[1 - g(\vec{k})]$ is very small (cf. Fig. 2). This is in contrast to the pure relaxation case (viz., $g(\vec{k}) = 1$), where for $\lambda \gg 6Q$, a motionally narrowed line is observed[26]:

$$\Phi(p) \approx \mathrm{Re}\left(\text{constant} \times \frac{1}{p - i\omega_0}\right) \tag{51}$$

(cf. Fig. 3). So the lesson is that even for a small

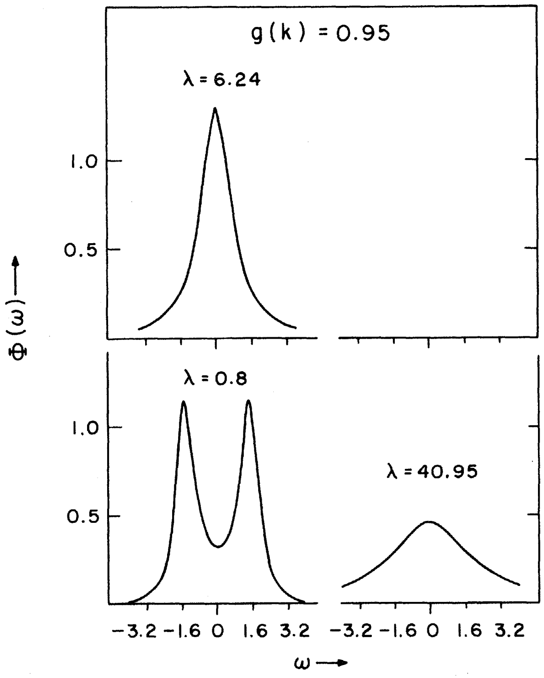

FIG. 2. Mössbauer line shape for different values of λ and for $g(k) = 0.95$ which corresponds to a jump length ~0.024 Å for the 14.4-keV γ ray from ^{57}Fe.

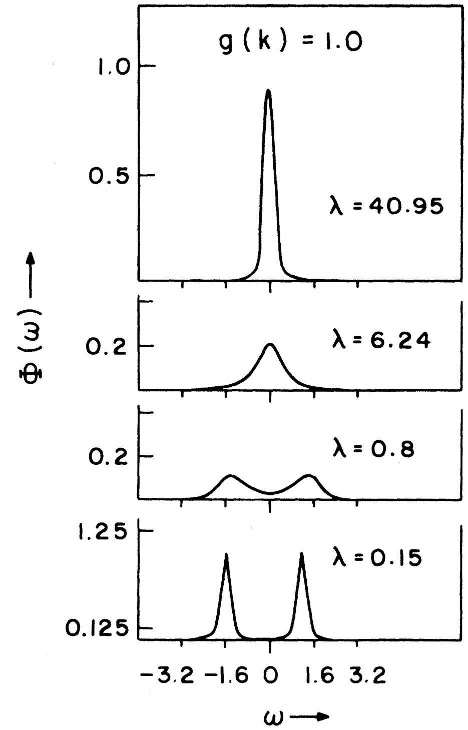

FIG. 3. Mössbauer line shape for different values of λ in the extreme case of $g(k) = 1.0$ which corresponds to a stationary nucleus. In this case, relaxation may be viewed to be caused by a fluctuating environment. For very large values of λ, a single motionally narrowed line is observed which feature is absent even in Fig. 2 although $g(k)$ is very close to 1.0.

but nonzero value of $[1 - g(\vec{k})]$, which is a measure of the phase change of the γ ray due to nuclear motion, the phenomenon of motional narrowing is not observed at all when the diffusion rate is very fast (cf. Fig. 2).

For interpretation of experimental results, it is instructive to have a feeling for the value of $g(\vec{k})$ in a real system. Let us consider two extreme cases.

1. Large jumps in random directions

Assuming that the nucleus can jump, from the center of a sphere of radius a to any point on its surface, we may set the probability of a single jump as

$$g(\vec{r}) = (1/4\pi a^2)\,\delta(r-a) \;, \tag{52}$$

where $r = |\vec{r}|$ and $4\pi a^2$ is a normalization factor for the probability.

From (27),

$$g(\vec{k}) = \sin ka/ka \;. \tag{53}$$

In a liquid like glycerol, the jump-distance is $a \approx 3$ Å.[27] So for the 14.4-keV γ ray from ^{57}Fe ($k = 7.3$ Å^{-1}),

$$g(\vec{k}) \approx 0.04 \;. \tag{54}$$

This corresponds approximately to a completely random-phase situation [cf. Eq. (48)]. The spectra obtained in this case as a function of the jump rate λ are similar to those given in Figs. 1 and 4.

While (52) may be a slight overestimate of the randomness of jumps in those liquids where diffusion takes place in large uncorrelated jumps, it is certainly incorrect in solids where the angle between successive jumps is determined by the crystal structure. Dibar-Ure and Flinn[28] have predicted a substantial correction to the liquidlike result (53) by considering jumps restricted by crystallographic directions in solids.

2. Extremely short jumps in random directions

In this case, $\vec{k}\cdot\vec{r} \ll 1$. This for ^{57}Fe yields a mean-jump distance $a \ll 0.137$ Å. Assuming spherical symmetry

$$g(\vec{r}) = g(r) \;,$$

and expanding $e^{i\vec{k}\cdot\vec{r}}$ in a power series in $\vec{k}\cdot\vec{r}$, we have

$$g(\vec{k}) = 1 - \tfrac{1}{6}k^2\langle r^2\rangle \;, \tag{55}$$

since $\int g(r)\,d\vec{r} = 1$ and the mean-square-jump distance

$$\langle r^2\rangle = \int r^2 g(\vec{r})\,d\vec{r} \;. \tag{56}$$

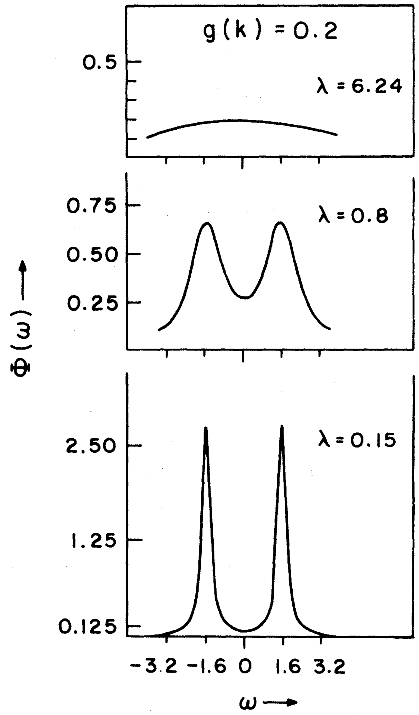

FIG. 4. Mössbauer line shape for different values of λ and $g(k) = 0.2$.

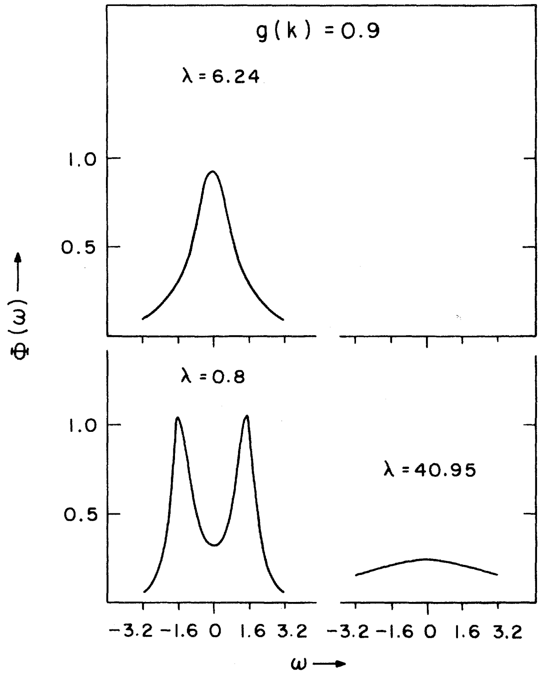

FIG. 5. Mössbauer line shape for different values of λ and for $g(k)=0.9$ which corresponds to a jump length ~ 0.11 Å.

From Eq. (46), the diffusion broadening in this case is given by

$$\Delta\epsilon = 2\lambda[1-g(\vec{k})] = 2Dk^2 \quad , \tag{57}$$

where the diffusion coefficient D is defined by

$$D=\tfrac{1}{6}\lambda\langle r^2\rangle \quad , \tag{58}$$

λ being the inverse of the mean time between two successive jumps. Equation (58) is the familiar Einstein relation for the self-diffusion coefficient obtained from a random-walk model.[29]

The expression (57) was also obtained by Singwi and Sjölander[4] in a continuous diffusion model where the single-jump probability $g(\vec{r})$ was assumed to satisfy a diffusion equation. In this case, Eq. (55) says that $g(\vec{k})$ is slightly smaller than one. But even though this difference [$g(\vec{k})=0.95$, for example] is small, a narrowing of the line is not to be observed in accordance with our discussion after Eq. (51). This is evident in Fig. 2. A value of $g(k)=0.95$ corresponds to a jump length of nearly 0.024 Å.

D. Computed spectra

In Figs. 1–5, we have presented a series of plot of the line shape for different values of $g(k)$ as a function of the jump rate λ. The horizontal scale is the same in all the figures, but the vertical scale is different for different values of λ in Figs. 1, 2, 4, and 5. The vertical scale however is the same in Fig. 3 for all values of λ. Also, in all the figures, the quadrupole splitting and the natural-ray linewidth are taken as $3Q=1.6$ mm/sec and $\Gamma=0.1$ mm/sec, respectively.[2] The quadrupole splitting in phosphoric acid is determined from the experimental spectra in the limit of zero relaxation, i.e., at very low temperatures.[2] Recent bulk diffusion measurements[30] in conjunction with Mössbauer work indicate that diffusion in phosphoric acid occurs via very short steps of length ~ 0.1 Å. This means that $g(k)$ should lie between 0.90 and 0.95 (cf. Figs. 2 and 5). Detailed comparison between the theoretical spectra presented here and the experimental results is underway now.[31]

VI. SUMMARY

We have treated here a model for Mössbauer line shape where relaxation occurs due to nuclear motion. The interplay of the effects of diffusion and relaxation was seen to yield interesting results depending on the degree of phase change because of nuclear motion. In the one extreme case when there is no phase change, we obtain the Blume result for pure relaxation effects. In the other extreme case of completely random-phase change, the theory yields the Singwi-Sjölander broadening of lines. So far we have found only one experimental situation involving Mössbauer measurements in phosphoric acid where the full significance of the theory is involved. It would be nice to see some more experiments; a few possibilities have been mentioned in Sec. I.

In Sec. V we have assumed that the directions of the electric field gradients at different sites are distributed at random. On the other hand, it is entirely possible in some liquids where diffusion occurs in the form of continuous motion that these directions are correlated to one another. The theoretical calculation in this case is a bit more complicated and is left for future work.

ACKNOWLEDGMENTS

The author is indebted to Professor P. A. Flinn for apprising him of the experimental work in phosphoric acid which motivated this theoretical study and for many fruitful conversations. He wishes to thank Professor S. L. Ruby for valuable correspondence about the experimental results. The author also acknowledges useful comments and encouragement from Professor M. Blume, Professor R. B. Griffiths, and Professor J. S. Langer.

[*] Research supported by Air Force Office of Scientific Research Grant No. 72-2311.

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