# Many-state relaxation model for the Mössbauer spectra of superparamagnets

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The stochastic relaxation theory of Anderson and Sack is applied to the Mössbauer spectra superparamagnetic particles with uniaxial anisotropy by including all possible values of the component of the magnetization along the quantization axis explicitly in the calculation. It is shown that for particles with a large number of states the Mössbauer line shape can be expressed directly in terms of the solution of a differential equation. Explicit solution of this equation in the low-temperature (high anisotropy barrier) approximation leads to effective relaxation rates between the two discrete allowed orientations of the magnetization. These rates are equivalent to those derived by Brown only if the relaxation matrix elements are assumed to have a certain rather arbitrary dependence on the temperature and magnetization.

## INTRODUCTION

The standard theory for the superparamagnetic relaxation of particles with uniaxial anisotropy[1] was derived by Brown[2–4] and refined by Aharoni.[5,6] Though all possible orientations of the magnetization with respect to the easy axis are considered in this theory, the final result is expressed in terms of relaxation between only those two states corresponding to the energy minima of the system. For particles with energies given by

$$E=-KV\cos^2\theta-HM_s\cos\theta\ , \tag{1}$$

where the magnetization $M_s=g\beta_e S$, $g$ is the electronic $g$ value, $\beta_e$ is the electronic Bohr magneton, $S$ is the total spin of the particle with volume $V$, $K$ is the anisotropy energy per unit volume, and $H$ is the externally applied magnetic field, the transition rates, in the low-temperature (high energy barrier) approximation, are

$$p_{12}=\frac{K\gamma_0}{M_s\pi^{1/2}}\alpha^{1/2}(1-h^2)(1+h)\exp[-\alpha(1+h)^2]\ ,$$
$$p_{21}(h)=p_{12}(-h)\ , \tag{2}$$

where $\alpha=KV/k_BT$, $h=HM_s/2KV$, and $\gamma_0$ is the gyromagnetic ratio. Mössbauer spectra are obtained from (2) by substitution into the standard expression for relaxation in a two-state system.

This rather specialized case of relaxation is, fortunately, exactly the expression required for many superparamagnets. The rapid transition from sextet to doublet which is observed,[1] with increasing temperature or decreasing volume is consistent with (2) when the pre-exponential factor is in the range $10^{10}$–$10^{12}$ s$^{-1}$. In this case the rates $p_{12}$ and $p_{21}$ pass very rapidly through the region $p\sim10^7$–$10^8$ s$^{-1}$, in which transitional spectra are observed as $T$, or $V$ is changed, for values of $k_BT$ typically in the region of $k_BT\sim0.1KV$.

The Brown theory is a rather indirect method of obtaining the Mössbauer line shape. By constraining the magnetization to lie near to the potential minima, phenomena such as collective excitations are excluded. For systems with rather small pre-exponential factors, say, $<10^{10}$ s$^{-1}$, the doublet-sextet transition occurs over a significant temperature range and transitional spectra become important. Since a significant range of orientations of the magnetization is now possible in the transition region, it is far from clear that a two-state relaxation model adequately describes the spectrum.

We present below an approach in which all possible orientations of the magnetization with respect to the quantization axis are included in the calculation of the Mössbauer line shape using the stochastic theory developed by Anderson,[7] expressed in a simplified form by Sack,[8] and first applied to Mössbauer spectra by Blume and Tjon.[9] The present model includes no assumptions similar to the random-phase approximation which was used by Dattagupta and Blume their treatment of superparamagnetism as a many-state relaxation problem.[10] We follow Brown, at least initially, in assuming that the interaction between the magnetization of the particle and the environment can be expressed in terms of a rapidly fluctuating random field. The new model contains one "free" parameter describing the strength of this field. We believe that questions concerning the functional dependence of the effective relaxation rate of a superparamagnet on the magnetization, temperature, and particle size can only be reliably answered by calculations of this parameter.

One apparent disadvantage of the Sack method is that for real superparamagnets it requires the inversion of large matrices of order $2S+1$, where $S$ might easily be several thousand. In practice there is no difficulty, as the inversion of the rather specialized matrices involved takes only $O(S)$ arithmetic operations, and for large $S$ the results converge reasonably rapidly for suitably scaled variables. In the limit of large $S$, the line shape can be expressed in terms of the solution of a second-order differential equation which is rather similar to the Fokker-Planck equation. The solution of this equation in the low-temperature limit gives effective relaxation rates between the two wells which can be made equivalent to

 

those obtained by Brown only by making rather arbitrary assumptions concerning the dependence of the parameter describing the random field on the temperature and magnetization. The solution of a finite but large matrix turns out to be an efficient way of solving the differential equation problem in the general case.

To make progress in what are potentially complicated calculations, we find it necessary to assume throughout this work that the nuclear Hamiltonian, which is fluctuating because of fluctuations in the magnetization, commutes with itself at different times. Methods involving Liouville superoperators for solving the combined stochastic–quantum-mechanical problem[11] are therefore unnecessary. We are therefore assuming either that the principal component of the electric field gradient $V_{zz}$ is equal to 0, and the anisotropy parameter for the quadrupole interaction $\eta'$ is equal to 0, or, most realistically, that $V_{zz} \ll H_{\rm int}$, where $H_{\rm int}$ is the hyperfine field and that a first-order perturbation treatment of the quantum-mechanical part of the problem is sufficient. The latter assumption is expected to be reasonably in most superparamagnets as the hyperfine field is typically larger than the quadrupole splitting.

The parameters of our many-state relaxation model are $K$, $V$, $T$, $M_s$, the strength of the random field, which may itself be a function of other parameters, and the static Mössbauer parameters. We introduce the many-state model with a discussion of two- and three-state relaxation systems, for which the results are well known.

## TWO- AND THREE-STATE RELAXATION MODELS OF SUPERPARAMAGNETISM

As we have assumed that the nuclear eigenstates are constant, the relaxation problem can be solved separately for each pair of lines (1 and 6, 2 and 5, and 3 and 4) in the static Mössbauer spectrum. We start from the expression first given by Sack:

$$I(\omega)=2\,\mathrm{Re}(\mathbf{W}\underline{M}^{-1}\mathbf{1})\,. \tag{3}$$

This is the general expression for the line shape $I(\omega)$ for a system which is undergoing Markov relaxation between $N$ different states. The $N$ components of the row vector $\mathbf{W}$ are proportional to the occupation probabilities of the states in equilibrium, 1 is a column vector with all components equal to unity and

$$\underline{M}=(i\omega+\Gamma)\underline{I}-i\Omega-\Pi \tag{4}$$

is a matrix containing the physical description of the system in terms of a set of line positions, the natural linewidth $\Gamma$, and the transition probabilities. $\Omega$ is a diagonal matrix with elements $\omega_i$, the line positions in the absence of relaxation, and $\Pi$ is given by

$$\Pi_{ij}=P_{ij},\quad \Pi_{ii}=-\sum_j P_{ij}\quad (i\neq j)\,, \tag{5}$$

where $P_{ij}$ is the transition probability per unit time per unit occupation of state $i$, from state $i$ to state $j$. All that is required to set up a relaxation problem for any number of states is a set of $W_{ij}$, and $\omega_i$, and $P_{ij}$. Thus for the two-state system the result can be expressed as[8]

$$I(\omega)=2\,\mathrm{Re}\left[\frac{(p_{21},p_{12})}{p_{21}+p_{12})}\begin{bmatrix} i(\omega-\delta)+p_{12}+\Gamma & -p_{12} \\ -p_{21} & i(\omega+\delta)+p_{21}+\Gamma \end{bmatrix}^{-1}\begin{bmatrix}1\\1\end{bmatrix}\right], \tag{6}$$

where for slow relaxation the lines are found at $\omega=\pm\delta$ according to the sign of the internal field ($2\delta$ is the magnetic hyperfine splitting between the pair of lines). The requirement for a Boltzmann population distribution in thermal equilibrium defines the relative magnitudes of $W_1$ and $W_2$ and the requirement that this population distribution is stable constrains $W_1p_{12}=W_2p_{21}$. The solution of (6) gives

$$I(\omega)=2\,\mathrm{Re}\left[\frac{i(\omega'+\eta\delta)+2p}{(\delta^2-\omega'^2)+2pi(\omega'-\eta\delta)}\right], \tag{7}$$

where

$$\omega'=\omega-i\Gamma\,,$$

$$\eta=(W_1-W_2)/(W_1+W_2)=(p_{21}-p_{12})/(p_{21}+p_{12})\,,$$

$$2p=p_{12}+p_{21}\,.$$

In general $I(\omega,\delta)$ must be added to $I(\omega,-\delta)$ since the nuclei are not themselves oriented by the field. The two-state model does not in itself provide a basis for a complete model of superparamagnetism since the parameter $p$ cannot be calculated without reference to states at the top of the energy barrier through which the system must pass to relax from state 1 to state 2.

Consider now a three-state model of superparamagnetism, in which the state with $S_z=0$, which for no applied field is at the top of the energy barrier, is included as well as those with $S_z=\pm S$. We arrange the states in order of increasing $S_z$, i.e, state 1 has $S_z=-S$, state 2 has $S_z=0$, and state 3 has $S_z=+S$.

When it is not mixed with the other states by relaxation, the state with $S_z=0$ gives a line at $\omega=0$. The situation is analogous to that in paramagnets—in slowly relaxing Fe(III), each of the three Kramers doublets give rise to separate component spectra with a splitting proportional to $|S_z|$. In real particles there may exist energy barriers around the "equator" of the particle, but if these are large enough to significantly localize the moment in a particular orientation so that a full hyperfine splitting is observed, then the particle anisotropy is not well described as uniaxial. An upper bound on the relaxation rates is provided by the requirement that for Markov relaxation, the response time of the particle must be longer than the correlation times of the random field, which is typically $\sim 10^{13}$ s.[3]

If we assume that relaxation between the states with $S_z=\pm S$ can only occur via $S_z=0$, as would be expected if

the relaxation is envisaged as a random walk of the magnetization vector with small step lengths, then there are just four relaxation rates to calculate in the three-state model, $p_{12}$, $p_{21}$, $p_{32}$ and $p_{23}$. The matrix $M$ is therefore tridiagonal. The intensities of the lines and hence the values of $W_i$ are given by the populations of the electronic states which give rise to each line. These can be found using Eq. (1). As with the two-state problem, the requirement that the equilibrium populations are given by the Boltzmann distribution provides constraints on the $p_{ij}$. Thus $W_1 p_{12} = W_2 p_{21}$ and $W_2 p_{23} = W_3 p_{32}$. We can therefore write

$$p_{12} = p' \exp\left[-\frac{\Delta E_{21}}{k_B T}\right], \quad p_{21} = p', p_{23} = p'', \quad p_{32} = p'' \exp\left[-\frac{\Delta E_{23}}{k_B T}\right], \tag{8}$$

where $\Delta E_{21}$ and $\Delta E_{23}$ are the (positive) energy differences between the relevant states. It is natural to put the temperature dependence of the rates into those transitions to higher energy, as to undergo these transitions the system must find the thermal bath defined by its environment with the required energy, whereas transitions to lower energy can occur regardless of the state of the bath. Alternative forms of (8) which still correspond to a Boltzmann distribution are possible. They lead to different results for the three-state model, but they leave unaffected the result for the many-state model, which is described below. If we assume that the temperature independent parts of the rates are determined by a random walk of the magnetization direction, then $p' = p''$ by symmetry. The expression corresponding to (2) is then

$$I(\omega) = 2\,\mathrm{Re}\left[\frac{(W_1, W_2, W_3)}{(W_1 + W_2 + W_3)} \begin{pmatrix} i(\omega-\delta)+\Gamma+\alpha p & -\alpha p & 0 \\ -p & i\omega+\Gamma+2p & -p \\ 0 & -\beta p & i(\omega+\delta)+\Gamma+\beta p \end{pmatrix}^{-1} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}\right], \tag{9}$$

where $W_i = \exp(-E_i/k_B T)$, $\alpha = \exp(-\Delta E_{21}/k_B T)$, $\beta = \exp(-\Delta E_{23}/k_B T)$.

In evaluating (9) it is convenient to postmultiply $M$ by the diagonal matrix whose elements are the reciprocal of the $W_i$ before inversion. The result is

$$I(\omega) = 2\mathrm{Re}\{i\{(-\beta\omega_0\omega_+ - \alpha\omega_0\omega_- - \alpha\beta\omega_+\omega_-) + ip[\beta(\alpha^2+2\alpha+2)\omega_+ + (\alpha^2+\beta^2)\omega_0 + \alpha(\beta^2+2\beta+2)\omega_-] + p^2(\alpha+\beta+\alpha\beta)^2\}\}[\omega_0\omega_+\omega_- - ip(\alpha\omega_0\omega_+ + \beta\omega_0\omega_- + 2\omega_+\omega_-) - p^2(\alpha\omega_+ + \beta\omega_- + \alpha\beta\omega_0)]^{-1}, \tag{10}$$

where $i\omega_0 = i\omega + \Gamma$, $i\omega_\pm = i(\omega \pm \delta) + \Gamma$. At low temperatures (10) can be simplified by neglecting $\alpha$ and $\beta$ compared to unity, to obtain

$$I(\omega) = 2\,\mathrm{Re}\left[\frac{-i}{(\alpha+\beta)} \frac{(\omega_0 - 2ip)(\beta\omega_+ + \alpha\omega_-) - p^2(\alpha+\beta)^2}{(\omega_0 - 2ip)(\omega_+\omega_-) - p^2(\alpha\omega_+ + \beta\omega_-)}\right]. \tag{11}$$

If then we assume $p \gg \omega$ in the region of interest, so $(2p + i\omega) \sim 2p$, the result is

$$I(\omega) = 2\,\mathrm{Re}\left[\frac{i(\omega_0 + \eta\delta) + p(\alpha+\beta)/2}{\delta^2 - \omega_0^2 + ip[(\alpha+\beta)/2](\omega_0 - \eta\delta)}\right], \tag{12}$$

where $\eta$, the net magnetization, is now $(\beta-\alpha)/(\beta+\alpha)$. This is exactly (7) with effective rates $p_{13} = \alpha p/2$ and $p_{31} = \beta p/2$. Physically, if the system is excited from state 1 to the state $S_z = 0$ at a rate $\alpha p$, relaxation down to states 1 and 3 occurs almost immediately, with a probability of 50% that the system ends up in a state different from the first. As a result of assumption (8), (11) has the same exponential form as Brown's equations (2) and for large $p$ it predicts a rapid doublet-sextet transition with temperature.

The three-state model has the potential advantage that it gives expressions for the line shape when the doublet-sextet transition occurs over an extended temperature range, i.e., when $p$ is comparatively small and the sextet-doublet transition takes place gradually as a function of temperature. However, the coexistence of sharp sextet and sharp doublet (or singlet) spectra, which is observed when the rate $p$ becomes very slow, can be explained entirely as a spurious result of allowing only discrete orientations. This is hardly a physically reasonable model of superparamagnetism.

There are also several problems relating to the definition of the three-state model. Firstly, $S_z = 0$ corresponds to the maximum electronic energy only in zero applied field. The intermediate state cannot be "moved" to an $S_z$ corresponding to the maximum electronic energy, since this would give a net magnetization even in the limit of fast relaxation, hence the model cannot give the correct dependence of the rate on the applied field. A method of calculating the dependence of $p$ on the particle size $V$ is also required. Brown's treatment showed that the shape of the potential well near both the minima and the maximum has an effect on the rate; a three-state model cannot include such factors. Finally, collective excitations are excluded as they were in the two-state model. All these problems are solved in the many-state model.

## THE MANY-STATE MODEL

Consider a particle of total spin $S$. All $(2S+1)$ possible values of $S_z$ can be included in the relaxation problem by increasing the dimension of the matrix $M$ to $(2S+1)$.

The relaxation rates between the various states can now be calculated directly as the squares of the quantum-mechanical matrix elements corresponding to the transitions. On the assumption that the forces causing relaxation can be represented by a random field perpendicular to the $z$ axis, the Boltzmann distribution independent parts of the transition probabilities are

$$r(S_z, S_z+1)=R\,|\langle S_z|S_-|S_z+1\rangle|^2 = R[S(S+1)-S_z(S_z+1)] \tag{13}$$

for adjacent $S_z$ states, and zero otherwise. The matrix $M$ therefore remains tridiagonal. $R$ is now a parameter proportional to the square of the random field; it determines the absolute rate of relaxation. The constancy of the parameter $R$ implies an effective "classical spin" for the environment.

The quantum-mechanical-transition probability (13) has a classical analog for large $S$. If the random field is imagined to cause the angle $\theta$ between the magnetization and the easy axis to undergo a random walk, then the rate of relaxation between configurations related by a small rotation $\delta\theta$ will be $\propto 1/(\delta\theta)^2$.

This angle is

$$\delta\theta=\cos^{-1}\left[\frac{S_z}{S}\right]-\cos^{-1}\left[\frac{S_z+1}{S}\right]=-\frac{1}{S}\frac{d}{dx}(\cos^{-1}x) = \frac{1}{(S^2-S_z^2)^{1/2}}\,, \tag{14}$$

which implies

$$r(S_z,S_z+1)\propto S^2-S_z^2\,,$$

which is equivalent to (13). $M$ can therefore be written

$$M_{kk}=i(\omega-\omega_k)+\Gamma-M_{kk-1}-M_{kk+1}\,,$$
$$M_{kk\pm1}=-r_{kk\pm1}[\exp(-\Delta E/k_BT)]\,, \tag{15}$$

where $k=1$ to $2S+1$, $k(S_z)=S_z+S+1$, and $r_{kk+1}$ and $r_{kk-1}$ are defined by (14), the exponential factor is included only for transitions to higher energy, and $\omega_k=(S-k+1)\delta/S$. The previous two- and three-state models correspond to (15) with $S=\frac{1}{2}$ and $S=1$.

The inverse of the matrix (15) is required for each value of $\omega$ in a simulated spectrum. One method of finding the inverse which has often been used for combined stochastic–quantum-mechanical problems,[12] is to note that since $M$ contains $\omega$ only as a multiple of the identity, the transformation which diagonalizes $M$ is independent of $\omega$. $M$ can therefore be diagonalized just once for each spectrum and then the calculation for each involves the simple inversion of a diagonal matrix. Unfortunately, diagonalization of matrices of order $N$ requires at $O(N^3)$ arithmetic operations and rapidly becomes impractical for $N$ greater than a few hundred.

We have found it efficient to calculate $I(\omega)$ for each $\omega$ using the standard Gauss-Jordan procedure, in which inversion is achieved by successive divisions of rows by their diagonal elements or "pivots" and subtractions of one row from another. The particular form of $M$ means that the diagonal elements of the transformed $M$ remain large compared to the off-diagonal elements, and therefore the method is stable without searches for suitable pivots. Since $M$ is tridiagonal, the number of computations in the calculation of the inverse is proportional to $N^2$. A further significant saving in computer time is obtained by noting that since $M^{-1}$ is postmultiplied by the column vector 1, only the sums of the rows of $M^{-1}$ are required.

Writing

$$\underline{M}^{-1}\mathbf{1}=\mathbf{V}\Rightarrow\underline{M}\mathbf{V}=\mathbf{1}\,, \tag{16}$$

The problem becomes a problem of solving a set of simultaneous equations for $\mathbf{V}$. As well as a large saving in storage requirements, the "inversion" now requires a number of operations which is proportional to $N$.

With this method, spectra for $S$ up to several hundred can be simulated with modest computers and on large systems inversion of matrices of order 1000–1000, corresponding to spins similar to those found in real systems, would be possible. However, it soon becomes apparent that very large calculations are not really necessary, as the computed spectra converge fairly rapidly with increasing $S$ as long as the ratios $k_BT$:$KV$:$S$ are kept constant. This convergence suggests that in the continuum limit, $I(\omega)$ can be expressed in terms of the solution of a differential equation.

## DERIVATION OF THE DIFFERENTIAL EQUATION FOR THE MÖSSBAUER LINE SHAPE

Each row of (16) gives an equation of the form

$$M_{k,k-1}V_{k-1}+M_{k,k}V_k+M_{k,k+1}V_{k+1}=1\,, \tag{17}$$

since $M$ is tridiagonal. The convergence for large matrix order $N$ suggests that in the limit of large $N$, $V_k$ can be assumed to form a continuous function $v(k)$ for which $v(k+dk)$ can be expanded as a Taylor series about $v(k)$. This gives

$$(M_{k,k-1}+M_{k,k}+M_{k,k+1})v_k+(M_{k,k+1}-M_{k,k-1})\frac{dv_k}{dk} + \left[\frac{M_{k,k+1}+M_{k,k-1}}{2}\right]\frac{d^2v_k}{dk^2}=1\,. \tag{18}$$

The expansion of $v$ must be taken to second order since, though successive differentials with respect to $k$ are smaller by $O(N)$ the coefficient of the $v'$ term may vanish. But, from (15), keeping only terms of highest order in $S$,

$$M_{k,k-1}+M_{k,k}+M_{k,k+1}=i(\omega-\omega_k)+\Gamma\,,$$
$$M_{k,k+1}-M_{k,k-1}=R\left[\frac{S^2-S_z^2}{k_BT}\frac{dE}{dk}+2S_z\right]\,, \tag{19}$$
$$M_{k,k+1}+M_{k,k-1}=-2R(S^2-S_z^2)\,,$$

where the result for the second equation, which involves an expansion of exponential of the energy, is independent of whether (8) or some alternative form is used. Changing to the variable $x=\cos\theta=(k-1-S)/S$ gives the differential equation

$$[i(\omega-\delta x)+\Gamma]v+R\left[(1-x^2)\frac{E'}{k_BT}+2x\right]\frac{dv}{dx}-R(1-x^2)\frac{d^2v}{dx^2}=1\ , \tag{20}$$

which is equivalent to

$$e^{\beta}\frac{d}{dx}[v'(1-x^2)e^{-\beta}]+\frac{1-[i(\omega-\delta x)+\Gamma]v}{R}=0 \quad \left[\beta=\frac{E}{k_BT}\right]\ . \tag{21}$$

This is exactly the Fokker-Planck differential equation derived by Brown except that we have a $[1-[i(\omega-\delta x)+\Gamma]v]/R$ term in place of Brown's $\lambda v$.[3] Changing variables to $\theta$ gives

$$\frac{d}{d\theta}\left[e^{-\beta\sin\theta}\frac{dv}{d\theta}\right]+\frac{e^{-\beta\sin\theta}}{R}\{1-[i(\omega-\delta\cos\theta)+\Gamma]v\}=0\ . \tag{22}$$

This form is useful since the potential which defines the problem is periodic and hence $v(\theta)=v(-\theta)$, therefore $dv/d\theta=0$ at $\theta=0,\pi$, whereas $dv/dx$ at these points is merely finite. The line shape is now

$$I(\omega)=\int_{-1}^{1}v(x)W(x)dx=\int_0^{\pi}v(\theta)W(\theta)\sin\theta d\theta\ . \tag{23}$$

Equation (22) becomes trivial in the limits of large and small $R$. As $R$ tends to zero, the requirement that $v'$ remains finite means that

$$v(\omega,x)=\frac{1}{\Gamma+i(\omega-\delta x)}\Rightarrow I(\omega)=\int_{-1}^{1}\frac{dxW(x)}{\Gamma+i(\omega-\delta x)}\ , \tag{24}$$

which is just a superposition of nonrelaxing lines. $v(\omega,x)$ is seen to be the absorption at $\omega$ per unit population of the state $x$. To solve for large $R$, it is useful to integrate (21) once and apply the boundary conditions; $v$ can be taken out of the integral since $v'$ tends to 0 for large $R$. This gives the expected result

$$v(\omega,x)=\frac{1}{\Gamma+i(\omega-\eta\delta)},\quad \eta=\frac{\int xW(x)dx}{\int W(x)dx}\ , \tag{25}$$

where $\eta$ is the magnetization.

In general the equation for $v(\omega,x)$ must be solved numerically and the inversion of the large matrices from which the differential equation was derived provides an efficient method of doing this. However, a good approximate solution where $k_BT<KV$ can be obtain using techniques similar to those used by Brown in the derivation of (2).

We start with the twice-integrated form of (21):

$$v(\theta)=v(0)+\int_0^{\theta}\frac{d\theta'}{R\sin\theta'}e^{\beta}\int_0^{\theta'}d\theta''e^{-\beta\sin\theta''}\{1-[i(\omega-\delta\cos\theta'')+\Gamma]v\}\ , \tag{26}$$

where the boundary condition $v'=0$ is already included. $v'(\pi)=0$, therefore

$$\int_0^{\pi}d\theta''e^{-\beta\sin\theta''}\{1-[i(\omega-\delta\cos\theta'')+\Gamma]v\}\equiv\int_0^{\pi}f(\theta'')d\theta''=0\ , \tag{27}$$

as in the derivation of (25). For small $T$ this integral is dominated by contributions from near the endpoints. Since $v'=0$ at the endpoints, $v$ changes very little in the range where the integrand is finite and can be taken outside the integral. This gives

$$\begin{aligned}&[1-(i\omega_-+\Gamma)v_0]I_1+[1-(i\omega_++\Gamma)v_\pi]I_2=0\\ &I_1=\int_0^{q}e^{-\beta\sin\theta}d\theta,\quad I_2=\int_{\pi-q}^{\pi}e^{-\beta\sin\theta}d\theta\end{aligned} \tag{28}$$

where $\omega_\pm=\omega\pm\delta$, $v_0=v(0)$, $v_\pi=v(\pi)$, and $q$ is some small number chosen to include the range over which the integrand is significant. Now, by assumption, $I(\omega)$ can now be written in the form

$$I(\omega)=(v_0I_1+v_\pi I_2)/(I_1+I_2)\ . \tag{29}$$

To find $I(\omega)$ we therefore need just one more equation in $v_0$ and $v_\pi$ to solve simultaneously with (28). The $\theta'$ integration provides this equation since

$$v_\pi-v_0=\int_0^{\pi}\frac{d\theta'e^{\beta}}{R\sin\theta'}\int_0^{\theta'}d\theta''f(\theta'')\ , \tag{30}$$

where $f(\theta'')$ is defined in (27). We have already noted that the $\theta''$ integral is dominated by its end points therefore

$$\begin{aligned}\int_0^{\theta'}d\theta''f(\theta'')&=-I_1((i\omega_-+\Gamma)v_0-1)\\&=I_2((i\omega_++\Gamma)v_\pi-1)=\alpha\ ,\end{aligned} \tag{31}$$

for all $q<\theta'<\pi-q$. But the $\theta'$ integral is dominated by its maximum since it contains $\exp(E/k_BT)$. The integral can be approximated by writing $E=E_m-E''\theta^2/2$ where $E''<0$, and replacing the limits by $\pm\infty$. If $\sin\theta$ is now replaced by its value at this maximum we obtain

$$v_\pi - v_0 = \frac{\alpha I_m e^{E_m/k_BT}}{R\sin\theta_m}, I_m = \int_{-\infty}^{\infty} \exp\left[\frac{E''(\theta')^2}{2k_BT}\right] d\theta' . \tag{32}$$

Solution of (28) and (32) simultaneously gives

$$v_0 = \frac{R' + a(i\omega_+ + \Gamma)}{R'[i(\omega - \eta\delta) + \Gamma] + a[\delta^2 + (\Gamma + i\omega)^2]}, \quad R' = \frac{R\sin\theta_m e^{-E_m/k_BT}}{I_m} \tag{33}$$

where $\eta = (I_1 - I_2)/(I_1 + I_2)$, is the magnetization [same as in expression (25)] and $a = I_1 I_2/(I_1 + I_2)$ and a similar equation for $v_\pi$. Substitution into the expression (28) for $I(\omega)$ gives

$$I(\omega) = \{R'(\Gamma + i(\omega - \eta\delta) + a[\delta^2 + (\Gamma + i\omega)^2]\} \times 2\,\mathrm{Re}[R' + ia(\omega + \eta\delta)] \tag{34}$$

But this expression is just (7) with $p = R'/2a$. We have therefore obtained expressions for the effective $p_{12}$ and $p_{21}$ for the system. For the $E(\theta)$ of equation (1) the values of the constants and integrals are

$$I_1 = \frac{k_BT}{2KV(1+h)} \exp\left[\frac{KV(1+2h)}{k_BT}\right],$$

$$I_2 = \frac{k_BT}{2KV(1-h)} \exp\left[\frac{KV(1-2h)}{k_BT}\right]$$

$$I_m = \left[\frac{\pi k_BT}{KV(1-h^2)}\right]^{1/2}, \quad \sin\theta_m = (1-h^2)^{1/2}, \tag{35}$$

$$h = \frac{HM_s}{2KV},$$

so that

$$p_{12} = \frac{R}{\sqrt{2\pi}}(1-h^2)(1+h)\left[\frac{2KV}{k_BT}\right]^{3/2} \times \exp\left[\frac{-KV}{k_BT}(1+h^2)\right]. \tag{36}$$

Equations (2) and (36) are equivalent for $R = (k_BT\gamma_0/2M_sV)$. The relationship between the two expressions can be shown by considering the derivation of (2) in more detail. (2) is obtained[3] from

$$p = h'\left[\frac{V}{2\pi k_BT}\right]^{1/2} (H_cM_s)^{3/2}(1+h)(1-h^2) \times \exp\left[-\frac{KV}{k_BT}(1+h)^2\right]$$

$$h' = \eta/(1/\gamma_0^2 + \eta^2M_s^2), \quad H_c = 2K/M_s, \tag{37}$$

by assuming $h'(\eta)$ has its maximum value, i.e., $\eta = 1/(\gamma_0 M_s)$ and $h' = \gamma_0/2M_s$. In the original paper[2] this assumption is justified by reference to the damping constants of "ordinary sized specimens." It is not necessarily applicable to microscopic particles. Another crucial parameter in Brown's theory is the diffusion constant $k'$, which is given by $k' = kTh'/V$. Our $R$ is therefore equivalent in some sense to Brown's diffusion constant, $k'$. The multistate relaxation method therefore gives the same result as Brown's method does with the assumptions that $k' = k_BT\gamma_0/2M_sv$ and critical damping. In the present model these assumptions appear rather arbitrary.

To make progress in predicting $R$ given $K$, $M_s$ and $T$ it would be necessary to consider the spin-lattice coupling process in more detail. We do not propose to do this here but we would note that the negative power of $T$ in the prefactor of (36) has the effect of making the doublet-sextet transition less sharp. However, spin-lattice interactions are generally proportional to $T$ raised to a power which may be quite large and which is almost certainly $> 1$. Brown's treatment may therefore tend to underestimate the sharpness of the Mössbauer double-sextet transition.

As $R$ increases the doublet-sextet transition occurs at increasingly low temperatures compared to $KV$, the low-temperature approximation becomes exact, and the spectra produced by the many state model become identical to those produced by the two-state model. Any distinction between the two models can in this case be made only after a quantitative calculation of absolute relaxation rates as a function of temperature, magnetization, and particle size becomes possible and the models are compared to experimental spectra. This will require the development of a theory for the microscopic interaction that couples the particle, with a large spin, to its environment. The interaction has in this paper been approximated by a classical random field but in reality may arise from spin-lattice relaxation of the paramagnetic type, magnon-phonon in-

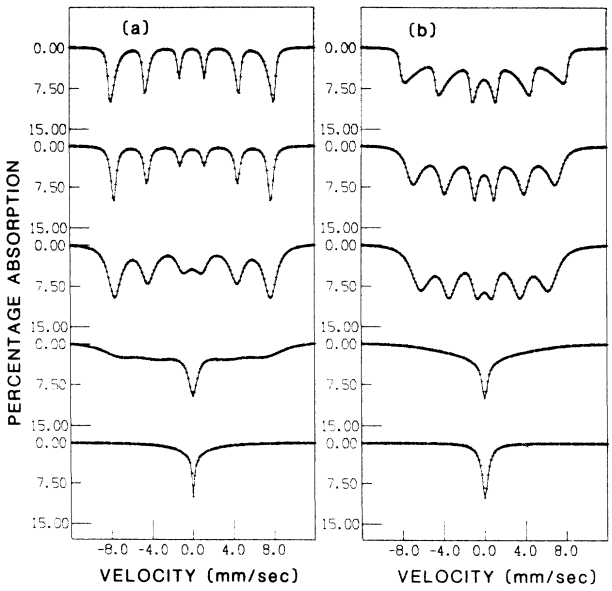


FIG. 1. Simulated spectra for the many-level relaxation model with parameters (a) $k_BT/KV = 0.1$, $R$ (from top to bottom) $= 0$, 100, 500, 2000, and 10000 mm s$^{-1}$; (b) $k_BT/KV = 0.5$, $R = 0.0$, 0.2, 1, 10, and 100 mm s$^{-1}$. The hyperfine field is 50 T throughout and $\Gamma = 0.4$ mm s$^{-1}$. Eighty levels have been used in the calculation.

teraction or magnon-magnon interaction or some combined process.[13]

The principle advantage of the many-state model is that it allows the magnetic interaction of the particle with environment to be expressed in terms of the above microscopic processes rather than the macroscopic "damping" and "diffusion" parameters found in Brown's model. Thus it is now possible in principle to derive for the first time a complete model of superparamagnetism including parameters describing the particle, its environment, and the coupling between them.

For $R=0$ the many-level model gives simply a distribution of internal fields. Spectra with $R\sim 1$ show a combination of field distribution and relaxation effects. Some typical spectra of this type are compared to those obtained with large $R$ in Fig. 1.

## CONCLUSION

A stochastic treatment of the Mössbauer lineshape gives additional insight into phenomena of superparamagnetic relaxation. Though the rates predicted by the new model are similar to those derived by Brown the differences are important. In the future it should be possible to calculate the random field parameter $R$ from the properties of the superparamagnetic particle and its environment in terms of transition probabilities calculated from matrix elements describing the interaction between the particle and its environment. This method may provide the answers concerning, for example, the difference between superparamagnetism in antiferromagnets and ferromagnets, which cannot be adequately answered by the Brown model.

[1]S. Morup, J. Magn. Magn. Mater. **37**, 39 (1983).
[2]W. F. Brown, J. Appl. Phys. **30**, 130S (1959).
[3]W. F. Brown, J. Appl. Phys. **34**, 1319 (1963).
[4]W. F. Brown, Phys. Rev. **130**, 1677 (1963).
[5]A. Aharoni, Phys. Rev. **135**, A447 (1964).
[6]A. Aharoni, Phys. Rev. **177**, 793 (1969)
[7]P. W. Anderson, J. Phys. Soc. Jpn. **9**, 316 (1954).
[8]R. A. Sack, Mol. Phys. **1**, 163 (1958).
[9]M. Blume and J. A. Tjon, Phys. Rev. **165**, 446 (1968).
[10]S. Dattagupta and M. Blume, Phys. Rev. B **10**, 4540 (1974).
[11]M. Blume, Phys. Rev. **174**, 351 (1968).
[12]D. C. Price, J. Phys. E **9**, 336 (1976).
[13]K. P. Sinha and N. Kumar, *Interactions in Magnetically Ordered Solids* (Oxford University Press, New York, 1980).