PHYSICAL REVIEW B VOLUME 35, NUMBER 3 15 JANUARY 1987-II

# Relaxation and nonradiative decay in disordered systems.
# III. Statistical character of Raman (two-quanta) spin-lattice relaxation

S. Alexander,* Ora Entin-Wohlman,† and R. Orbach
*Department of Physics, University of California, Los Angeles, California 90024*

(Received 30 July 1986)

Vibrational-mode localization leads to a statistical distribution $\mathscr{P}(W)$ for the (two-quanta) Raman spin-lattice relaxation rate, $W \equiv 1/T_1$. The characteristic function of the distribution and the cumulant moments are calculated. The time dependence of the recovery of the magnetization after saturation is obtained. It is shown that the observed Raman spin-lattice relaxation rate should exhibit a "staircaselike" structure. The length of the "steps" is random and their slope is proportional to the square of the temperature $T^2$. The steps are centered about the average value of $W$. A procedure is suggested for analyzing experimental data in a manner which will exhibit these features, if present. Observation of these predictions will serve as proof that localized vibrations contribute to the spin-lattice relaxation process.

## I. INTRODUCTION

We have previously investigated[1-4] the effect of localization of vibrational modes on (electronic or nuclear) spin-lattice relaxation processes[5] in disordered materials. Our calculations were general, applying to phonons, localized in the Anderson[6] sense, and to fractons, localized in the Ioffe-Regel[7] sense. We have argued previously[8-10] that the high-frequency modes in such materials are strongly localized fractons obeying anomalous power laws, both in the dispersion and in the density of states (the so-called "fracton" model).

In Refs. 1 and 2, we discussed the direct, or single vibrational quanta relaxation process, and in Refs. 3 and 4 the two vibrational quanta (Raman) relaxation process. In both cases, the distribution of local environments leads to a broad distribution $\mathscr{P}(W)$ of the relaxation rate $W$. This is reflected in nonexponential decay profiles $S(t)$ for the sum over all sites. We were able to calculate these decay profiles for both direct and Raman relaxation processes. Our calculations would be relevant to disordered materials where the (electronic or nuclear) spins were randomly distributed relative to the positions of the vibrational states. Examples would be glasses, gels, or polymeric materials. While $S(t)$ was found to be very sensitive to the localization of the vibrational quanta, the *average* relaxation decay profile (appropriate for strong cross relaxation) was found to be exponential. The associated average relaxation rate mirrors the vibrational density of states and the indices characterizing the localized wave functions.

Our purpose here is to examine a different aspect of the same problem—namely, the character of the relaxation rate at a *specific* site. The decay profile of single-site spin-lattice relaxation is always exponential. However, as we shall show in detail below, the temperature dependence does not simply follow that of the *average* relaxation rate. Instead, we shall exhibit irregular statistical fluctuations in the spin-lattice relaxation rate temperature dependence, reflecting the specific environment of the chosen site. As the temperature is raised, new relaxation channels, involving higher-frequency localized vibrations, will become activated, adding to the relaxation processes responsible for the relaxation at lower temperatures.

The temperature dependence of the relaxation rate, $W(T)$, for a specific site is of course unique and well defined. Our statistical analysis will show that the curves for $W(T)$ at different sites will fluctuate with strong correlations in the temperature dependence between them, underlying large accumulative fluctuations.

This calculation will also be relevant to materials where the (electronic or nuclear) spins all have the same spatial relationship to the vibrational states. An example would be electronic centers in proteins, such as those investigated by Stapleton and co-workers.[11] In these experiments, the paramagnetic ion (low-spin Fe) always occupies a well-defined specific site in the large and complicated molecule. Our calculations statistically predict the structure of the temperature dependence of the relaxation rate for such an experiment. Comparison with such experiments can therefore serve as a test of the validity of a fracton quasirandom model for the vibrational states of a protein molecule.

To perform the calculation, we shall use a step function approximation for the vibrational Bose functions. This will obviously exaggerate the sharpness of the fluctuations occurring when new relaxation channels come into play. Within this approximation the relaxation rate has a $T^2$ temperature dependence between randomly spaced steps which occur when new relaxation channels are opened (see, for example, the inset to Fig. 1). The full Bose functions will obviously smooth out these steps without, however, qualitatively changing the "devil's staircase" structure of the $W(T)$ curves. We shall use the results of Ref. 3 and a generating function technique[12-14] to analyze the statistical properties of these curves.

In Refs. 3 and 4 we restricted out calculation to the contribution of the most effective largest relaxation rate channel. In Secs. II and III we generalize this result by calculating the full multisite decay profile directly. This amounts to a generating function technique for the mo-

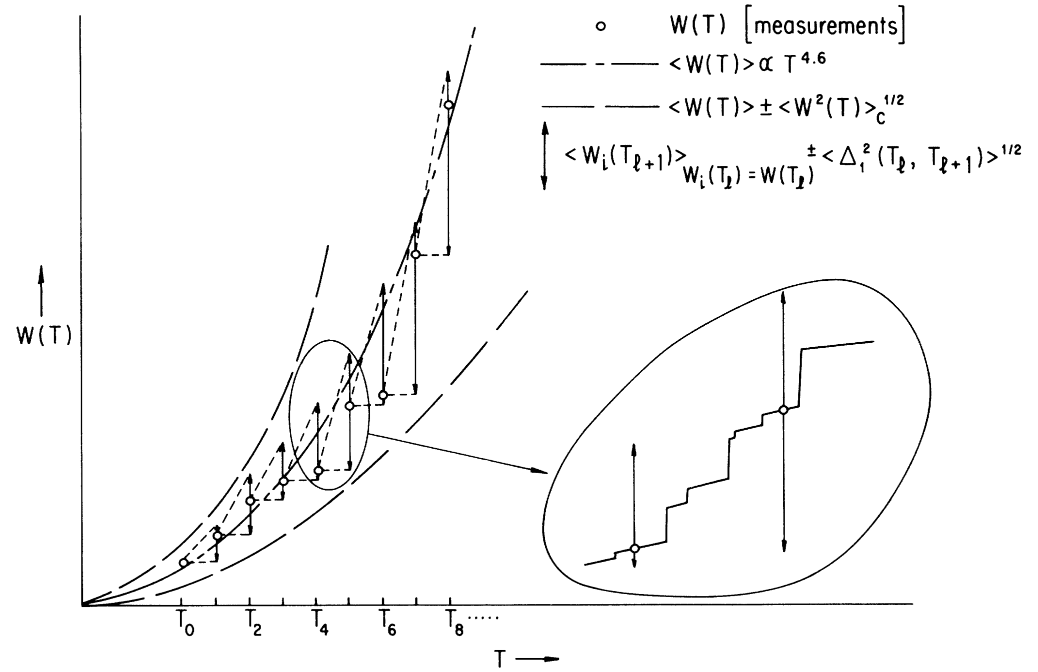

FIG. 1. Predicted temperature dependence of the measured relaxation rate at a specific site $\ell$, using the step function approximation for the Bose functions. The drawing assumes $a = 5.6$ [see Eq. (28) for the definition of $a$]. The measurement of the spin-lattice relaxation time at each temperature $T_l$, $W(T_l)$, is denoted by an open circle and *predicts* the range in which one expects to find $W(T_{l+1})$. This range is represented in the figure by the vertical arrows. At each step, $W(T_{l+1})$ was chosen randomly within this range, leading to the values of $W$ (open circles) exhibited in the figure. For comparison, we also show the temperature dependence of the *average* spin-lattice relaxation rate, $\langle W(T)\rangle$, with its associated error limits, $\pm\langle W^2\rangle_c^{1/2}$. The assumption made in construction of this figure is that the intervals between actual measurements, $T_{l+1}-T_l$, are large compared to the spacings of the individual "steps" in $W$ [see the discussion leading to Eq. (41)]. The inset shows a (conceivable) plot of steps within a single interval, should the measurements be made on a scale fine with respect to the step size.

ments of the distribution $\mathcal{P}(W)$, and allows us to include all relaxation channels (not just the one giving the largest relaxation rate seen at a given site). In Sec. III we also derive explicit expressions for the short and asymptotic long time decay, and for the moments in the fracton model.

In Sec. IV we consider the implications of the statistical character of the relaxation rate upon the measured temperature dependence of $W$. We show that the statistical distribution of the relaxation channels produces a "staircase" shape for the increase of $W$ with increasing temperature. The length of the steps is random, and their slope is proportional to $T^2$. Observation of these predictions may have occurred,[15] although the interpretation is not unambiguous. The discussion in Sec. IV does not depend upon the particular model for the vibrational-mode localization, applying to both localized phonons and fractons. Section V summarizes our results.

## II. RELAXATION RATE DISTRIBUTION

In two recent papers[3,4] we considered the spin-lattice relaxation of a localized magnetic center (either electronic or nuclear) resulting from a Raman process with two localized vibrational modes. For a change of magnetic energy small compared to the temperature (or to the vibrational energies involved in the relaxation process), the absorption of a mode of energy $\omega$ spatially centered at a distance $L$ from the magnetic center, and the emission of a second mode of essentially the same energy, but centered a distance $L'$ from the magnetic center, one finds a spin-lattice relaxation rate equal to

$$W(\omega,L,L') = W_m(\omega)\exp[-(L/l_\omega)^{d_\phi} - (L'/l_\omega)^{d_\phi}] . \tag{1}$$

Here, $l_\omega$ is the localization length characterizing the wave function of the localized vibrational mode of energy $\omega$, and $d_\phi$ is the exponent determining the strength of the "super-localization."[16] The temperature dependence is contained in $W_m(\omega)$, which includes the vibrational-mode occupation numbers. The explicit forms of $l_\omega$ and $W_m(\omega)$, as well as the value of $d_\phi$, will be discussed in the following section.

Let us now calculate the probability of finding a pair of vibrations that gives rise to the relaxation rate, Eq. (1). It consists of two factors: (i) The probability of finding a mode with energy between $\omega$ and $\omega + d\omega$ located at a distance between $L$ and $L + dL$ away from the magnetic center:

$$N(\omega) D L^{D-1} d\omega\, dL . \tag{2}$$

Here, $N(\omega)$ is the vibrational-mode density of states and

$D$ is the mass distribution dimension [i.e., $D=d$ for localization in Euclidean space or the fractal (mass) dimension for fractal geometry]. (ii) The probability of finding the second mode, of energy between $\omega$ and $\omega+\delta$, a distance between $L'$ and $L'+dL'$ away from the magnetic center:

$$N(\omega)D(L')^{D-1}\delta dL' . \tag{3}$$

The energy width $\delta$ represents the combined width of the localized-mode eigenstates. We assume that it is determined by some other relaxation process affecting the vibrational system (e.g., anharmonic interactions) and that it is independent of $\omega$, $L$, and $L'$. One may also consider a situation where $\delta$ is given by the relaxation rate itself,[1,2] in which case a self-consistent calculation of the relaxation rate is required. This possibility complicates the calculation greatly and will not be considered further here.

The probability density for finding two modes that yield the relaxation rate $W(\omega,L,L')$ is

$$G(\omega,L,L')dL\,dL'\,d\omega = [N(\omega)D]^2\delta L^{D-1}(L')^{D-1}dL\,dL'\,d\omega . \tag{4}$$

We now construct the relaxation rate distribution, $\mathscr{P}(W)$. For ease of notation, we define

$$z=(L/l_\omega)^{d_\phi},\quad \eta=D/d_\phi . \tag{5}$$

The probability for finding a pair of vibrational modes with the first member located at $z$ and the second at $z'$, such that $z'>z$, is

$$F(z)=\int_z^{z_v}dz'\int d\omega\, G(\omega,z,z') , \tag{6}$$

where, from Eqs. (4) and (5),

$$G(\omega,z,z')=\delta[N(\omega)l_\omega^D]^2\eta^2z^{\eta-1}(z')^{\eta-1} . \tag{7}$$

In Eq. (6), $z_v$ is the largest available distance from the magnetic center, and the $\omega$-integration bounds depend upon the physical situation. They will be specified later.

From Eq. (6) we find that the probability that there is no vibration pair available for relaxation in the entire system is

$$\exp\left[-\int_0^{z_v}dz\,F(z)\right] .$$

The contribution to the probability $\mathscr{P}(W)$ for this condition is

$$\mathscr{P}_0(W)=\exp\left[-\int_0^{z_v}dz\,F(z)\right]\delta(W) , \tag{8}$$

where $\delta(W)$ is the $\delta$ function. When there is just one vibrational pair available for relaxation in the entire system, the contribution to the probability $\mathscr{P}(W)$ for this condition is

$$\mathscr{P}_1(W)=\exp\left[-\int_0^{z_v}dz\,F(z)\right]\int_0^{z_v}dz_1\int_{z_1}^{z_v}dz_1'\int d\omega_1 G(z_1,z_1',\omega_1)\delta[W-W(\omega_1,z_1,z_1')] . \tag{9}$$

Here, the exponential factor is a product of three exponentials:

$$\exp\left[-\int_0^{z_v}dz\,F(z)\right]=\exp\left[-\int_0^{z_1}dz\,F(z)\right]\exp\left[-\int_{z_1}^{z_1'}dz\,F(z)\right]\exp\left[-\int_{z_1'}^{z_v}dz\,F(z)\right] , \tag{10}$$

where

$$\exp\left[-\int_{z_a}^{z_b}dz\,F(z)\right]$$

ensures that there is no mode available in the spatial region $\{z_a,z_b\}$. In a similar manner, we can write down the contribution for $l$ channels ($l$ pairs of vibrations) to the distribution $\mathscr{P}(W)$:

$$\mathscr{P}_l(W)=\exp\left[-\int_0^{z_v}dz\,F(z)\right]\int_0^{z_v}dz_1\int_{z_1}^{z_v}dz_1'\int d\omega_1\, G(z_1,z_1',\omega_1) \times\cdots\times\int_0^{z_v}dz_l\int_{z_l}^{z_v}dz_l'\int d\omega_l G(z_l,z_l',\omega_l)\delta\left[W-\sum_{l_1=1}^{l}W(\omega_{l_1},z_{l_1},z_{l_1}'\right] . \tag{11}$$

The probability density for the relaxation rate is given by the sum of the terms appearing in Eq. (11),

$$\mathscr{P}(W)=\sum_{l=0}^{\infty}(1/l!)\mathscr{P}_l(W) , \tag{12}$$

where the factorial has been introduced to avoid double counting. In constructing $\mathscr{P}(W)$, we have neglected the effect of level repulsion and the contributions arising from four (or more) vibrational modes of the same energy.

As is more usually the case,[12–14] it is more convenient to consider the characteristic function of the distribution $f(k)$, rather than the distribution $\mathscr{P}(W)$, itself. Noting that $\mathscr{P}(W)$ is normalized, we find

$$f(k)=\int dW\,\mathscr{P}(W)\exp(-ikW)=\exp\left[\int_0^{\infty}dz\int_z^{\infty}dz'\int d\omega\, G(z,z',\omega)(\{\exp[-ikW(\omega,z,z')]\}-1)\right] , \tag{13}$$

where we have put $z_v$ (corresponding to the maximum spatial dimension of the system) equal to infinity. Using the cumulant expansion theorem,

$$\mathscr{f}_c(k) = \ln \mathscr{f}(k) = \langle [\exp(-ikW)] - 1 \rangle_c$$
$$= \sum_{l=1}^{\infty} [(-ik)^l / l!] \langle W^l \rangle_c \ , \tag{14}$$

where $\mathscr{f}_c(k)$ is the cumulant characteristic function of $\mathscr{P}(W)$ and $\langle W^l \rangle_c$ is the $l$th cumulant. Explicitly,

$$\begin{aligned} &\langle W \rangle_c = \langle W \rangle \ , \\ &\langle W^2 \rangle_c = \langle (W - \langle W \rangle)^2 \rangle \ , \\ &\langle W^3 \rangle_c = \langle (W - \langle W \rangle)^3 \rangle \ , \\ &\ldots , \end{aligned} \tag{15}$$

where $\langle W^l \rangle$ denotes the $l$th moment of the distribution $\mathscr{P}(W)$.

The cumulants $\langle W^l \rangle_c$ are thereby given by [using Eqs. (1), (5), (7), and (14)]

$$\langle W^l \rangle_c = \int_0^{\infty} dz \int_0^{\infty} dz' \, \eta^2 z^{\eta-1} (z')^{\eta-1} \exp[-l(z+z')]$$
$$\times \int d\omega \, \delta [N(\omega) l_\omega^D]^2 W_m^l(\omega) \ . \tag{16}$$

The $z,z'$ integrations are straightforward, leading to

$$\langle W^l \rangle_c = (\eta/2) \Gamma(\eta) \Gamma(\eta+1) (1/l)^{2\eta}$$
$$\times \int d\omega \, \delta [N(\omega) l_\omega^D]^2 W_m^l(\omega) \ , \tag{17}$$

where $\Gamma(\eta)$ is the $\Gamma$ function.

The first cumulant gives the average relaxation rate, $\langle W \rangle = 1/T_1^{\text{ave}}$. The second cumulant yields the mean-square deviation of $W$ from its average value. Thus, $\langle W^2 \rangle_c$ measures the width of the distribution function for the relaxation rate. The time dependence of the recovery of the magnetization after saturation, $S(t)$, is given by the Laplace transform of the distribution $\mathscr{P}(W)$. Hence, substituting $k \rightarrow -it$, it can be obtained from the expression for the characteristic function $\mathscr{f}(k)$, given by Eq. (13). That is,

$$S(t) = \mathscr{f}(k) \,|_{k \rightarrow -it} \ . \tag{18}$$

It follows that at short times, such that $W_m(\omega) t < 1$, only the first cumulant contributes to $\mathscr{f}(-it)$. From Eq. (15) this leads to an exponential form for $S(t)$:

$$S(t) \propto \exp(-\langle W \rangle_c t) \equiv \exp(-\langle W \rangle t), \quad W_m(\omega) t < 1 \ . \tag{19}$$

At longer times, when $W_m(\omega) t > 1$, one has to take account of the full cumulant expansion, Eq. (14). This is very cumbersome; in particular, because $\eta$ as given by Eq. (5) is not necessarily an integer. We can, however, evaluate the long-time behavior of $S(t)$ directly.

Inserting $k \rightarrow -it$ into Eq. (13), we find

$$\ln S(t) = \int_0^{\infty} dz \int_z^{\infty} dz' \int d\omega \, G(z,z',\omega) (\{\exp[-tW(\omega,z,z')]\} - 1)$$
$$= \int d\omega \, \delta [N(\omega) l_\omega^D]^2 \int_0^{[W_m(\omega)t]^{1/2}} dy (\ln\{[W_m(\omega)t]^{1/2}/y\})^{\eta}$$
$$\times \int_0^{y} dy' (\ln\{[W_m(\omega)t]^{1/2}/y'\})^{\eta} (1 - yy') \exp(-yy') \ , \tag{20}$$

where we have made use of Eqs. (1), (5), and (7). For $W_m(\omega) t \gg 1$, the limiting behavior of Eq. (20) is

$$\ln S(t) \simeq -\int d\omega \, \delta [N(\omega) l_\omega^D]^2 (\tfrac{1}{2})^{2\eta+1} \{\ln [W_m(\omega) t]\}^{2\eta} \ ,$$
$$W_m(\omega) t \gg 1 \ . \tag{21}$$

Equations (17) and (21) generate the principal results for the Raman relaxation rate arising from two localized vibrational modes. We apply these results to a particular form of localized vibrations, fractons, in the next section.

## III. RAMAN RELAXATION RATE DISTRIBUTION FOR FRACTONS

Fractons are characterized[8–10] by (i) the fracton density of states:

$$N_{\text{fr}}(\omega) = (\bar{\bar{d}} \omega^{\bar{\bar{d}}-1}) / (\Omega_{fD}^{\bar{\bar{d}}} a_0^D) \ , \tag{22}$$

where $\bar{\bar{d}}$ is the fracton dimensionality, $a_0$ the microscopic length scale, and $\Omega_{fD}$ the maximum ("Debye") fracton energy; condition (ii), unique to fractons, relates the fracton energy to the localization length:

$$l_\omega = a_0 (\omega / \Omega_{fD})^{-\bar{\bar{d}}/D} \ . \tag{23}$$

The fractons are defined over length scales $L$ such that $a_0 < L < \xi$, where $\xi$ is a *maximum* length scale beyond which the system appears homogeneous. Consequently, there exists a *minimum* fracton frequency, $\omega_c$. From Eq. (23),

$$\omega_c = \Omega_{fD} (\xi / a_0)^{-D/\bar{\bar{d}}} \ . \tag{24}$$

Equations (17) and (21) contain the factor $N_{\text{fr}}(\omega) l_\omega^d$. Using Eqs. (22) and (23),

$$N_{\text{fr}}(\omega) l_\omega^D = \bar{\bar{d}} / \omega \ . \tag{25}$$

Hence, the integrations in Eqs. (17) and (21) will be dominated by fracton frequencies near the bottom of the fracton energy range. This is opposite that for phonon-induced Raman relaxation (or for localized phonon-induced Raman relaxation, when the localization length is only weakly dependent upon the phonon energy). In these cases, the more rapid increase of $N_{\mathrm{ph}}(\omega)$ with frequency $[N_{\mathrm{ph}}(\omega)\propto\omega^{d-1}$, where $d$ is the Euclidean or "embedding" dimension—compare with Eq. (22)] means that high energy $(\sim k_B T/\hbar)$ phonons dominate the contribution to the relaxation integral.

The energy and temperature dependence of $W_m(\omega)$ [see Eq. (1)] has been derived elsewhere.[3,4] The result is

$$W_m(\omega)=\gamma^4(\omega/\Delta^2)^2(\omega/\Omega_{fD})^{4q-2}(l_\omega/a_0)^{-2D}(1/\delta)\times\{\exp(\beta\omega)/[\exp(\beta\omega)-1]^2\}\ . \tag{26}$$

Here, $\gamma$ is the coupling constant between the magnetic center and the lattice vibrations, $\Delta$ is the energy between the ground magnetic state and the first excited magnetic state coupled by the spin-vibration interaction,[5] and

$$q=\bar{\bar{d}}d_\phi/D\ . \tag{27}$$

The energy width $\delta$ appears in Eq. (26) because of the discrete character of the (localized) fracton modes, and replaces the energy conserving $\delta$ function in the usual golden rule expression [see the discussion after Eq. (3)]. Equation (26) exhibits the form of the relaxation rate for Kramers transitions[5] (relaxation occurring between time-reversed magnetic states of half integral spin). For non-Kramers transitions, the factor $\omega/\Delta^2$ in Eq. (26) is replaced by $1/\Delta$.

As noted above, the largest contribution to the relaxation integral arises from fracton frequencies $\omega\sim\omega_c$. At temperatures much greater than $\omega_c$, we can approximate the Bose function combination appearing in Eq. (26) by $(\beta\omega)^{-2}$, and set the upper bound for the integration equal to $1/\beta$. Then, $W_m(\omega)$ varies with $\omega$ as $\omega^{a-2}$, where

$$a=4q+2\bar{\bar{d}}=4\bar{\bar{d}}(d_\phi/D)+2\bar{\bar{d}}\ . \tag{28}$$

For percolating networks in $d=3$, the exponents appearing in Eq. (28) result in $a=5.63$ for Kramers transitions and $a=3.63$ for non-Kramers transitions. Inserting Eq. (26) into Eq. (17), we find

$$\langle W^l\rangle_c=(\eta/2)\Gamma(\eta)\Gamma(\eta+1)(1/l)^{2\eta}[l(a-2)-1]^{-1}\times\bar{\bar{d}}^{\,2}\beta\delta\left[\frac{1}{\delta}\left(\frac{\gamma}{\Delta}\right)^4\frac{\Omega_{fD}^{2-a}}{\beta^a}\right]^l,\quad \beta\omega_c>1\ . \tag{29}$$

We see that the average relaxation rate $(l=1)$ is independent of the fracton energy width $\delta$, and varies with temperature as $(k_BT)^{a-1}$. As shown in the preceding section, the time dependence of the magnetization recovery at short times is linear [Eq. (19)], with a decay rate given by the average relaxation rate. This behavior will prevail for times such that $W_m(1/\beta)t\ll 1$, equivalent to

$$\left[\frac{1}{\delta}\left(\frac{\gamma}{\Delta}\right)^4\left(\frac{\Omega_{fD}^{2-a}}{\beta^a}\right)\right]t\ll 1\ . \tag{30}$$

The temporal behavior at much longer times is given by Eq. (21), in combination with Eq. (26). We find

$$\ln S(t)=-\bar{\bar{d}}^{\,2}(\tfrac{1}{2})^{2\eta+1}\beta\delta[W_m(1/\beta)t]^{1/(a-2)}(\Gamma\{2\eta+1,[1/(a-2)]\ln[W_m(\omega_c)t]\}-\Gamma\{2\eta+1,[1/(a-2)]\ln[W_m(1/\beta)t]\})\ , \tag{31}$$

where $W_m(1/\beta)$ and $W_m(\omega_c)$ are the values $W_m(\omega)$ takes at the upper and lower bound of fracton energy integration, respectively, and $\Gamma(\alpha,z)$ is the incomplete $\Gamma$ function. One finds from Eq. (31)

$$\ln S(t)\sim-\beta\delta[W_m(1/\beta)t]^{1/(a-2)}\ ,\quad W_m^{-1}(\omega_c)>t>W_m^{-1}(1/\beta)\ , \tag{32a}$$

$$\ln S(t)\sim-(\delta/\omega_c)\{\ln[W_m(\omega_c)t]\}^{2\eta},\quad t>W_m^{-1}(\omega_c)\ . \tag{32b}$$

Thus, the time dependence response of the magnetization in the "near" long-time regime is of a stretched exponential form [Eq. (32a)], while in the "far" long-time regime it varies faster than any power law, but slower than an exponential or a stretched exponential [Eq. (32b)]. We note that the exponent of Eq. (32a) differs from that exhibited for the same time regime in Refs. 3 and 4. The latter is in error, and is the result of a saddle-point approximation.

These results, Eq. (32), complete our treatment of the time-dependent response of the magnetization, $S(t)$. We should point out that Eq. (32) includes *all* of the two-fracton relaxation channels. Our previous results, found in Refs. 3 and 4, are limited to only the largest (dominant) two-fracton relaxation channel. In addition, Eq. (32) has been derived in a much more transparent fashion than our original expressions in Refs. 3 and 4.

## IV. SINGLE-SITE RELAXATION

The results of the preceding sections involve averaging over all fracton configurations around the relaxing spin. In most situations this is what one would expect to measure because the spins are distributed randomly in the structure, with locally inequivalent and uncorrelated environments (note that one is also neglecting cross relaxation).

A specific single spin does have, of course, a well-defined environment. That is, there are well-defined locations for all fractons at all distances $L,L'$. It will therefore decay exponentially with a well-defined $W(T)$ determined by its environment. The disorder will become apparent through the temperature dependence for $W(T)$, at any specific site, which is predicted to have rather complex correlated fluctuations (see below). Only the average over all such sites will exhibit the simple smooth temperature dependence predicted above in Eq. (29):

$$\langle W \rangle \propto T^{2\bar{\bar{d}}[1+2(d_\phi/D)]-1}, \quad \text{Kramers transitions ;} \tag{33a}$$

$$\langle W \rangle \propto T^{2\bar{\bar{d}}[1+2(d_\phi/D)]-3}, \quad \text{non-Kramers transitions.} \tag{33b}$$

A specific magnetic site will have many different Raman channels available for spin-lattice relaxation. Because of the Bose factors, only those channels for which $k_B T \geq \omega$ (with $\omega$ the fracton frequency) are effective for relaxation at any given temperature $T$. For simplicity in our discussion, we shall replace the Bose factor in Eq. (26) by a step function

$$\exp(\beta\omega)/[\exp(\beta\omega)-1]^2 \simeq \begin{cases} (\beta\omega)^{-2}, & \beta\omega < 1 , \\ 0, & \beta\omega > 1 . \end{cases} \tag{34}$$

This is not a very good description in detail, but it will greatly simplify the calculation and will allow us to analyze how the emergence of new active relaxation channels affect the temperature dependence of the spin-lattice relaxation rate. We emphasize that the sharpness of the "steps" in our results (inset to Fig. 1) reflects the approximation, Eq. (34). The full Bose factors would still exhibit a staircaselike structure, but with rounded-off corners.

Each open channel makes a contribution to the relaxation rate of magnitude

$$W_m(\omega) \propto \exp(\beta\omega)/[\exp(\beta\omega)-1]^2 \propto T^2 . \tag{35}$$

The quantity to calculate is the number of such channels active at a given temperature.

Let the experiment be one where the spin-lattice relaxation time is measured at a series of temperatures $T_l$, $T_{l+1}$, etc., ($T_{l+n} < T_{l+n+1}$). Assume that one measures a value of the relaxation rate, $W(T_l)$, at a given temperature $T_l$. As the temperature is increased from $T_l$ to $T_{l+1}$, those channels which contributed to $W(T_l)$ at temperature $T_l$ will continue to contribute, but with a contribution $(T_{l+1}/T_l)^2$ larger than at temperature $T_l$. This gives rise to a systematic increase in the relaxation rate: given a configuration of relaxation channels which are active at $T_l$, yielding $W(T_l)$ at that temperature, then at temperature $T_{l+1}$ this configuration will contribute $(T_{l+1}/T_l)^2[W(T_l)]$ to the relaxation rate. This behavior is illustrated in Fig. 1.

In addition to this systematic increase, there is also a random increase, obeying a statistical distribution, *independent* of the value of $W(T_l)$. This random increase arises from the new relaxation channels which become active at temperatures between $T_l$ and $T_{l+1}$. It is a statistical contribution because of the (assumed) spatial randomness of the vibrational-mode locations relative to the spatial position of the relaxing magnetic center. These additional relaxation channels will result in a rapid increase in $W$, ending one step but beginning another with a larger "leading edge" value of $W$. This is seen in the inset to Fig. 1 as the staircaselike structure for $W(T)$.

It follows that, given that the relaxation rate is $W(T_l)$ at temperature $T_l$, the relaxation rate at the (higher) temperatures $T_{l+1}$ is given by

$$W(T_{l+1}) = (T_{l+1}/T_l)^2 W(T_l) + \delta W(T_{l+1},T_l) . \tag{36}$$

The first term on the right-hand side of Eq. (36) represents the systematic change of $W$ with temperature, while the second describes the random increase caused by the opening of new relaxation channels between the temperatures $T_l$ and $T_{l+1}$.

The random quantity $\delta W(T_2,T_1)$ has a conditional probability density, which we denote by $\mathcal{Q}$. In constructing an equation for $\mathcal{Q}$ in terms of the probability density $\mathcal{P}$, we note that, on the one hand, the relaxation channels contributing to $\mathcal{P}(W;T)$ range from the lower-frequency cutoff $\omega_c$ up to $T$. On the other hand, the relaxation channels contributing to $\mathcal{Q}$ come from the frequency interval between $T_1$ and $T_2$. Therefore,

$$\mathcal{P}(W;T_{l+1},\omega_c) = \int dW' \mathcal{P}(W';T_l,\omega_c)\mathcal{Q}(\delta W;T_{l+1},T_l) , \tag{37}$$

where, from Eq. (36),

$$\delta W = W - (T_{l+1}/T_l)^2 W' ,$$

and we have explicitly included the relevant frequency range as a pair of parameters in the probability densities $\mathcal{P}$ and $\mathcal{Q}$. It follows that the moments of the probability density $\mathcal{Q}$ are those of $\mathcal{P}$, Eq. (17), with the frequency integration ranging from $T_l$ up to $T_{l+1}$. This means that the second cumulant [Eq. (17)] gives the temperature dependence for the increase in the width of the distribution for $\delta W$. Explicitly, inserting Eq. (26) into Eq. (17), setting $l=2$, and integrating from $T_l$ to $T_{l+1}$, we find

$$\langle \delta W^2(T_{l+1},T_l) \rangle_c \propto T_{l+1}^4 (T_{l+1}^{2a-5} - T_l^{2a-5}) . \tag{38}$$

In order to make explicit the implications of this result for experiment, we return to Eq. (36). Subtract from $\delta W$ its average value. Denoting

$$\begin{aligned} \Delta_1(T_{l+1},T_l) &= \delta W(T_{l+1},T_l) - \langle \delta W(T_{l+1},T_l) \rangle \\ &= \delta W(T_{l+1},T_l) - [\langle W(T_{l+1}) \rangle - (T_{l+1}/T_l)^2 \langle W(T_l) \rangle] , \end{aligned} \tag{39}$$

we find,

$$\begin{aligned} &W(T_{l+1}) - \langle W(T_{l+1}) \rangle \\ &\quad = (T_{l+1}/T_l)^2 [W(T_l) - \langle W(T_l) \rangle] + \Delta_1(T_{l+1},T_l) . \end{aligned} \tag{40}$$

Squaring Eq. (40) and averaging, one sees that the square of the deviation of $W(T_{l+1})$ from the average value $\langle W(T_{l+1}) \rangle$ depends upon the difference between $W(T_l)$ and $\langle W(T_l) \rangle$ from a previous measurement, as well as upon the random variable $\Delta_1(T_{l+1},T_l)$. Hence, there is a nonrandom correlation from measurement to measurement as the temperature is increased, and one must, for example, be careful when performing a least-squares analysis of the experimental data to extract $\langle W(T)\rangle$.

Any specific site $\ell$ should exhibit this correlated staircase behavior. The average of $W_\ell(T)$ [$W_\ell(T)$ being the relaxation rate of site $\ell$] over all sites is of course $\langle W(T)\rangle$. However, for the *specific* site $\ell$, we know that we measure $W_\ell(T_l)$ which is in general $\neq\langle W(T_l)\rangle$. The average rate at temperature $T_{l+1}$, averaged over all sites ($\ell$) for which $W_\ell(T_l)=W(T_l)$, is not $\langle W(T_{l+1})\rangle$ but rather the conditional average

$$\langle W_\ell(T_{l+1})\rangle_{W_\ell(T_l)=W(T_l)} =\langle W(T_{l+1})\rangle+(T_{l+1}/T_l)^2[W(T_l)-\langle W(T_l)\rangle] \; . \tag{41}$$

Because of these implicit correlations, it is not correct to determine the temperature dependence of the average relaxation rate $\langle W(T)\rangle$ (which among other things reflects the density of vibrational states) by fitting it directly to the measured curve $W(T)$. The experiment cannot be regarded as a direct measurement of $\langle W\rangle$, but rather as a measurement of a correlated temperature dependence with averages at each stage given by Eq. (29) for $l=1$. A proper analysis of the experiments requires that this correlation be taken into account.

To be specific, assume that $W(T)$ has been measured at temperatures $T_0,T_1,T_2,\ldots,T_l,\ldots,T_N$. The proper quantity to be minimized in the analysis of the experimental data is not the usual

$$\sum_l [W(T_l)-\langle W(T_l)\rangle]^2$$

because the deviations $W-\langle W\rangle$ are not statistically independent. A correct procedure requires that the correlations be removed. The simplest method for so doing is to minimize the sum of differences,

$$\sum_l [\Delta_1^2(T_l)/(T_{l+1}-T_l)^2]=(\{W(T_{l+1})-\langle W(T_{l+1})\rangle-(T_{l+1}/T_l)^2[W(T_l)-\langle W(T_l)\rangle]\}/(T_{l+1}-T_l))^2 \; , \tag{42}$$

for which the quantities in the curly brackets are predicted to be statistically independent.

Writing the average relaxation rate in a concise form [see Eq. (29) for $l=1$],

$$\langle W(T)\rangle=W_0(k_BT/\Omega_{fD})^{a-1} \; , \tag{43}$$

we find

$$\langle W(T_{l+1})\rangle-(T_{l+1}/T_l)^2\langle W(T_l)\rangle \simeq[(T_{l+1}-T_l)/T_l](a-3)\langle W(T_l)\rangle \; . \tag{44}$$

Similarly,

$$W(T_{l+1})-(T_{l+1}/T_l)^2W(T_l) =W(T_{l+1})-W(T_l)-2[(T_{l+1}-T_l)/T_l]W(T_l) . \tag{45}$$

Inserting Eqs. (44) and (45) into Eq. (40), we obtain

$$\sum_{l=1}^{N}\Delta_1^2(T_l,T_{l-1})/(T_l-T_{l-1})^2=\sum_{l=1}^{N}\{[W(T_l)-W(T_{l-1})]/(T_l-T_{l-1})-(2/T_{l-1})W(T_{l-1}) +[(a-3)/T_{l-1}]\langle W(T_{l-1})\rangle\}^2 \; . \tag{46}$$

Thus, as described above, to determine $\langle W(T)\rangle$ from a series of measurements of $W(T)$ at temperatures $T_0,T_1,T_2,\ldots,T_l,\ldots,T_N$, one should minimize the right-hand side of Eq. (46) with respect to $a$ (to obtain the temperature dependence) and $W_0$ (to obtain the magnitude) [see Eq. (43)].

Note that the only quantity peculiar to fractons in this result is the index $a$ [Eq. (28)]. For localized phonons in the Anderson sense (Euclidean space), $a=4+2d$. Thus, our results apply to both characters of localized vibrational states, fractal and Euclidean.

## V. SUMMARY AND CONCLUSIONS

We have treated the statistical features of the Raman spin-lattice relaxation process involving two localized vibrational states. Applying the procedure to fractons, we have calculated the time dependence of the recovery of the magnetization, incorporating all relaxation channels (and not just the largest channel, as in previous treatment[3,4]). We have shown that an experimental plot of $W(T)$ versus $T$ should not be a simple power law, but instead should reflect the random positions of the vibrational modes relative to the magnetic site. A staircase structure is predicted with ever widening heights to the various steps. We have been able to calculate the mean-square departure of the measured $W(T)$ from its average value, $\langle W(T)\rangle$. Because of the correlation which exists between the measurement of $W(T)$ at one temperature and its measured value at another temperature, we have had to outline a procedure for experimentally determining $\langle W(T)\rangle$. We await experiments which measure the spin-lattice relaxation rate of localized magnetic centers embedded in fractal networks. Examples can be found in Stapleton's measurements of $1/T_1(T) \equiv W(T)$ for low spin iron in biological molecules.[11] There are apparent fluctuations in his published data which are reminiscent of Fig. 1. However, there may be systematic errors in his data, because of averaging methods, which could be responsible for these departures from simple power-law behavior.[15]

We hope these calculations will stimulate investigations of $1/T_1(T) \equiv W(T)$ for electronic or nuclear centers in materials which could exhibit fractonlike vibrational excitations.

## ACKNOWLEDGMENTS

This research was supported by the National Science Foundation under Grant No. DMR-84-12898, and by the Fund for Basic research administered by the Israel Academy of Sciences and Humanities.

---

[*] Permanent address: Racah Institute of Physics, The Hebrew University of Jerusalem, 91 904 Jerusalem, Israel.

[†] Permanent address: School of Physics and Astronomy, Tel-Aviv University, Ramat-Aviv, 69 978 Tel-Aviv, Israel.

[1] S. Alexander, Ora Entin-Wohlman, and R. Orbach, J. Phys. (Paris) Lett. **46**, L-549 (1985).

[2] S. Alexander, Ora Entin-Wohlman, and R. Orbach, Phys. Rev. B **32**, 6447 (1985).

[3] S. Alexander, Ora Entin-Wohlman, and R. Orbach, J. Phys. (Paris) Lett. **46**, L-555 (1985).

[4] S. Alexander, Ora Entin-Wohlman, and R. Orbach, Phys. Rev. B **33**, 3935 (1986).

[5] R. Orbach and H. J. Stapleton, *Electronic Paramagnetic Resonance*, edited by S. Geschwind (Plenum, New York, 1972), p. 121.

[6] S. John, H. Sompolinsky, and M. J. Stephen, Phys. Rev. B **27**, 5592 (1983).

[7] A. F. Ioffe and A. R. Regel, Prog. Semicond. **4**, 237 (1960).

[8] S. Alexander and R. Orbach, J. Phys. (Paris) Lett. **43**, L-625 (1982).

[9] S. Alexander, C. Laermans, R. Orbach, and H. M. Rosenberg, Phys. Rev. B **28**, 4615 (1983).

[10] S. Alexander, Ann. Isr. Phys. Soc. **5**, 144 (1983).

[11] H. J. Stapleton, J. P. Allen, C. P. Flynn, D. G. Stinson, and S. Kurtz, Phys. Rev. Lett. **45**, 1456 (1980); J. P. Allen, J. T. Colvin, D. G. Stinson, C. P. Flynn, and H. J. Stapleton, Biophys. J. **38**, 299 (1982); J. T. Colvin and H. J. Stapleton, J. Chem. Phys. **82**, 4699 (1985); P. J. Muench and H. J. Stapleton, *ibid.* **82**, 2828 (1985); G. C. Wagner, J. T. Colvin, J. P. Allen, and H. J. Stapleton, J. Amer. Chem. Soc. (to be published).

[12] M. Inokuti and F. Hirayama, J. Chem. Phys. **43**, 1978 (1965).

[13] D. L. Huber, Phys. Rev. B **31**, 6070 (1985).

[14] S. K. Ma, *Statistical Mechanics* (World Scientific, Singapore, 1985).

[15] H. J. Stapleton (private communication).

[16] Y.-E. Levy and B. Souillard (unpublished).