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Relaxation and nonradiative decay in disordered systems. I. One-fracton emission

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Relaxation processes are calculated for the emission and absorption of localized vibrational quanta by a localized electronic state. Vibrational localization can be geometrical in origin (as on a fractal network, with fractons being the quantized vibrational states) or as a consequence of scattering (analogous to Anderson localization, with localized phonons being the quantized vibrational states). The relaxation rate is characterized by a probability density which is calculated here for both classes of localization for two extreme limits: (a) the sum of the electronic and vibrational energy widths independent of the spatial distance between the electronic and vibrational states, and (b) the sum of the energy widths equal to the relaxation rate itself. The time profile of the initial electronic state population is calculated for both cases. The profile for interaction with fractons for case (a) is proportional to $t^{-c_1(\ln t)^{(D/d_\phi)-1}}$, where c_1 is a constant, D is the fractal dimensionality, and d_ϕ is defined by the range dependence of the fracton wave function: $\phi \propto \exp(-r^{d_\phi})$. This decay is faster than any power law but slower than exponential (or stretched exponential). The time profile for the interaction with fractons for case (b) is proportional to $\mathrm{const}+c_2(1/t)(\ln t)^{(D/d_\phi)-1}$, where c_2 is another constant. This expression shows that some sites do not relax in this limit. The average relaxation rate is calculated for both cases, along with its frequency and temperature dependence.

I. INTRODUCTION

There are theoretical reasons to believe that the higher-frequency vibrational modes in disordered systems are localized.[1-6] The origin of the localization could be either the relatively weak effect of impurity scattering, analogous to Anderson localization,[4] or the more dramatic effects one expects from a fractal description of geometric disorder in the short-range disordered regime.[1-3] In the latter case, we refer to the vibrational modes as fractons. The vibrational density of states is strongly modified from the Debye form, and the localization length shows a strong, power-law, dependence on frequency.[1] Experimental checks of these predictions are not easy, and heretofore have been necessarily indirect. We have shown elsewhere[6] that prominent features of the low-temperature specific heat and of the thermal conductivity of amorphous materials appear to support a fractal interpretation for the higher-energy vibrational excitations.

Our purpose in this paper is to discuss the effect of the localization of vibrational modes on relaxation processes involving the emission and absorption of vibrational quanta by a localized electronic state. Such processes are, of course, extensively encountered in electron-spin-resonance experiments, and in the nonradiative decay or recombination of electronic excitations.

When the vibrational modes are phonons, the theory of these processes is standard and well understood.[7] We shall show that the modifications in the vibrational spectrum because of disorder can lead to quite dramatic changes which have direct experimental implications. The most striking will be the modification of the relaxation profile which we shall show to be nonexponential. This is a direct result of vibrational localization which breaks the equivalence between electronic sites. In addition, there are effects on the temperature and frequency dependence of the average (integrated) relaxation rate.

Our aim in this paper is twofold. On the one hand, we believe we provide a better and more realistic description of relaxation phenomena in disordered materials. Experimental results of the type we predict are quite common and should be compared with a more adequate theory than is at present available. On the other hand, the interpretation of these experiments should provide a fairly sensitive and detailed check into the character of the vibrational spectrum.

We shall discuss in this paper the analog of the single-phonon relaxation process: the decay of a localized excitation by the emission of a single localized vibrational quantum (a fracton). The main effect of localization is on the relaxation time profile. Different spatial sites can have very different relaxation rates because of their distance from the closest suitable relaxing vibration. The result is a strongly nonexponential decay. We also consider the frequency and temperature dependence of the average relaxation rate and the results of cross relaxation. A brief preliminary report of our main results has appeared elsewhere.[8]

In two companion papers we shall discuss related problems. Relaxation by a two-quantum (Raman) vibrational process is very common, and in particular usually dominant at higher temperatures for electron-spin resonance. We shall discuss the somewhat more complex effects of vibrational localization on these processes in a forthcoming publication[9] (a brief preliminary report of our main results has appeared elsewhere[10]). A second paper will discuss the relaxation of extended electronic excitations when the disorder has a large effect on the vibrations.[11]

Physically, the dominant effect of the localization of the vibrational states is to introduce differences in the relaxation rate between one electronic site and another. This is because single-quantum relaxation requires a localized vibration of suitable energy. Different sites of the relaxing excitation are therefore not equivalent. At some sites the relaxation rate is rapid because a suitable vibration is centered close by. For others, the closest energy-conserving vibration is spatially far away, and the relaxation is very slow. The dominant effect is the distance to the closest suitable excitation.

In Sec. II we derive an expression for the relaxation rate due to the emission of a localized vibration centered at a distance L from the localized electronic site. We do this both for fractons and for (Anderson) localized phonons. In general, there are many parallel relaxation channels available. We calculate in Sec. III the probability distribution for the largest relaxation channel, arising from the closest resonant localized lattice vibration. We assume that this dominates the relaxation and calculate the resulting time decay profile in Sec. IV. We show in the Appendix that the contributions coming from relaxation rates smaller than the largest (i.e., from localized lattice vibrational modes further away from the electronic site) introduce, at the most unfavorable case, logarithmic corrections which have no practical import for the long-time behavior. The statistical analysis is similar to that used in some related problems such as spatial diffusion,[12] variable-range hopping in one dimension,[13] and optical quenching on fractal structures.[14] A peculiar feature of our problem is the importance of the combined electronic and vibrational states energy-level width (δ). When the width is independent of L, one finds a decay slower than any exponential (or stretched exponential), but faster than any power law. When the relaxation itself provides the dominant broadening mechanism, one must perform a self-consistent analysis. One finds that the line splits into narrow and broad components. The latter decays as a power law in time. We also calculate the average decay rate and its frequency and temperature dependence.

The derivations contained in Secs. II—IV are carried out for (localized) fracton vibrational states. We show how these results can be carried over to localized phonon vibrational states in Sec. V. There we compare the energy dependence of the average relaxation rate for the two situations. Section VI contains our conclusions and suggestions for experiments which should exhibit properties calculated in this paper.

II. THE ONE FRACTON RELAXATION RATE AT A GIVEN SITE

The dynamical interaction with a vibration is proportional to the local strain ($\nabla \mathbf{u}$). In principle, one would need to know the details of the normalized (fracton) wave function $[\phi_\alpha(\mathbf{r})]$,

$$u_\alpha(\mathbf{r}) \propto \phi_\alpha(\mathbf{r}) , \tag{1}$$

where $u_\alpha(\mathbf{r})$ is the amplitude at $\mathbf{r}$ of mode α (frequency ω_α) centered at the origin. We make two assumptions:

$$| \nabla\phi(\mathbf{r}) | \propto \omega^q \phi(\mathbf{r}) , \tag{2}$$

where the numerical value of the exponent q, the energy index, is unity for phonons, but can be different for fractons. Further, we assume exponential localization

$$[\phi_\alpha(L)]^2 \simeq (l_{\omega_\alpha})^{-D} \exp[-(L/l_{\omega_\alpha})^{d_\phi}] , \tag{3}$$

where l_{ω_α} is the localization length at frequency $\omega=\omega_\alpha$, d_ϕ is a geometrical exponent describing the fact that even an exponential decay (in some measure) on the fractal[15] will be distorted in real space, and D is the fractal dimension. In general, $1 \le d_\phi \le d_{\min}$, where $d_{\min}$ is defined[16] by $l \propto R^{d_{\min}}$, and l is the shortest path between two points separated by a Pythagorean distance R. We are unable to be more specific at this time, and therefore must regard d_ϕ as a parameter whose value can be obtained from explicit simulations on fractal networks. In the Euclidean limit, $d_\phi = d_{\min} = 1$. For fractons, we further assume that l_ω is the only relevant length in the problem (replacing the wavelength for phonons), so that

$$l_\omega \propto \omega^{-\bar{\bar{d}}/D} , \tag{4}$$

where $\bar{\bar{d}}$ is the fracton dimension. Taking the gradient in Eq. (2) and using Eq. (1) for the fracton wave function, we find $q = \bar{\bar{d}}(d_\phi/D)$ upon using Eq. (4). We shall describe localized phonons by setting $q = d_\phi = 1$, $D=3$ (the dimension of space) in Eqs. (2) and (3), and replacing l_ω [Eq. (4)] by a localization length ξ assumed to be frequency independent.

We now use the "golden rule" to write down the transition probability per unit time for an electron to change its state to one which differs from the initial state by an energy ω_0, caused by its interaction with a fracton of the same energy centered a distance L away. A straightforward generalization of the calculation of the direct process relaxation rate (as found, for example, in Ref. 7) yields

$$W(\omega_0,L) \propto \omega_0^{2q-1} l_{\omega_0}^{-D} \coth(\beta\omega_0/2) \times \frac{1}{\delta_L} \exp[-(L/l_{\omega_0})^{d_\phi}] . \tag{5}$$

Here ω_0^{2q} arises from the spatial derivative of the wave function, ω_0^{-1} results from the normal-mode expansion, $l_{\omega_0}^{-D}$ from the normalization of the wave function [see Eq. (3)], and $\coth(\beta\omega_0/2)$ is the fracton occupation number. The exponential factor in Eq. (5) describes the wave-function localization. The factor δ_L represents the energy width of the fracton state. When the vibrational state is extended (i.e., for phonons in the usual sense), one would find[7] an energy-conserving delta function in place of $1/\delta_L$. The quantity δ_L will be shown (below) to play a very important role in the calculation of electronic relaxation via the electron-fracton interaction.

The fracton energy width, δ_L, originates either through vibrational anharmonic coupling, or through the electron-fracton interaction itself. The anharmonic contribution to the energy width arises from two principal channels:

$$\text{fracton}+\text{phonon}\rightarrow\text{fracton}$$

and

$$\text{fracton}\rightarrow\text{phonon}+\text{phonon}\ .$$

These processes have been calculated very recently in the context of the fracton "hopping" contribution to the heat conductivity of a fractal network.[17] Their explicit values depend upon the fracton energy, the crossover frequency ω_c, and other material parameters of the medium. In general, they will not depend upon L, the distance between the localized electron and the center of the fracton wave function. Thus, under conditions when the anharmonic interaction dominates the contribution to δ_L, one can set $\delta_L=\delta$.

When the anharmonic contribution is less than the electronic relaxation rate caused by the electron-fracton interaction, one replaces the former by the latter—that is, one replaces δ_L by the relaxation rate itself. This means that the presence of δ_L in the expression for the relaxation rate [Eq. (5)] will lead to a self-consistent determination of the relaxation rate. In addition, the electron-fracton interaction depends upon the distance L between the electronic state and the center of the fracton wave function. This will require explicit consideration of the L dependence of δ_L in the calculation of $W(\omega_0,L)$ [Eq. (5)], and will further complicate the evaluation of $W(\omega_0,L)$.

In summary, we shall consider both limiting cases in this paper: the fracton anharmonic width larger and smaller than $W(\omega_0,L)$. However, intermediate situations can obtain wherein $W(\omega_0,L)$ will be smaller for large L than the anharmonic width, but larger for smaller L. This turns out not to complicate our calculation greatly [see the discussion after Eq. (19)].

We rewrite Eq. (5) in the form

$$W(L)=W_{\max}(\delta_0/\delta_L)\exp[-(L/l_{\omega_\alpha})^{d_\phi}]\ , \tag{6}$$

where the maximum relaxation rate is defined as

$$W_{\max}\propto\omega_0^{2q-1}l_{\omega_0}^{-D}\coth(\beta\omega_0/2)/\delta_0\ .$$

This is the relaxation rate for a fracton centered at the origin.

III. THE PROBABILITY DISTRIBUTION FOR THE LARGEST ELECTRONIC RELAXATION RATE

We first construct the probability density $\bar{P}(W)$ for a certain relaxation rate at a given electronic state. We then use it to derive the probability density $P(W)$ that W is the largest relaxation rate at that electronic site.

The probability $\bar{P}(W)$ consists of (i) the probability that there is a fracton level with energy in the range ω_0, $\omega_0+\delta_L$ centered on the fractal at a distance between L and $L+dL$ from the electronic site:

$$N_{\text{fr}}(\omega_0)\delta_L D L^{D-1}dL\ , \tag{7a}$$

where $N_{\text{fr}}(\omega)$ $(\propto\omega^{\bar{\bar{d}}-1})$ is the fracton vibrational density of states,[1] and (ii) a delta function requiring the electronic relaxation rate $W(\omega_0,L)$ caused by the fracton centered a distance L away to be equal to W:

$$\delta(W(\omega_0,L)-W)\ . \tag{7b}$$

Integrating over all L, we obtain

$$\bar{P}(W)=\int dL\,L^{D-1}DN_{\text{fr}}(\omega_0)\delta_L\delta(W(\omega_0,L)-W)\ . \tag{8}$$

From Eq. (8) we can construct the probability that there is no relaxation rate larger than W as seen from a given electronic site:

$$\prod_{W\le W'\le W_{\max}}[1-\bar{P}(W')dW']=\exp\left[-\int_W^{W_{\max}}dW'\bar{P}(W')\right]. \tag{9}$$

Finally, the probability density $P(W)$ that W is the largest relaxation rate is

$$P(W)=\bar{P}(W)\exp\left[-\int_W^{W_{\max}}dW'\,\bar{P}(W')\right]\ . \tag{10}$$

Note that one expects $P(W)$ to be normalized ($\int P(W)dW=1$) while $\bar{P}(W)$ counts all relaxation channels and is not normalized. We now evaluate $P(W)$ for the two cases described above.

(a) *Levels with a constant energy width.* Writing $\delta_L=\delta_0=\delta$ in Eq. (6) and inserting into Eq. (8), we find

$$\bar{P}_{(\text{a})}(W)\,dW=c_1(D/d_\phi)[\ln(W_{\max}/W)]^{(D/d_\phi)-1}dW/W\ , \tag{11}$$

where

$$c_1(\omega_0,\delta)=N_{\text{fr}}(\omega_0)(l_{\omega_0})^D\delta\ . \tag{12}$$

We note that the geometrical exponent d_ϕ, defined in Eq. (3), appears only through the combination D/d_ϕ. The value of this ratio will in general depend upon the Euclidean dimensionality, but is always ≥ 1. This will assist us in the derivation of $P(W)$.

Inserting Eq. (11) into Eq. (10), we obtain the probability density for the largest W:

$$\begin{aligned}P_{(\text{a})}(W)=\;&c_1(D/d_\phi)[\ln(W_{\max}/W)]^{(D/d_\phi)-1}\\&\times\exp\{-c_1[\ln(W_{\max}/W)]^{D/d_\phi}\}/W\ .\end{aligned} \tag{13}$$

This probability density is normalized to unity, exhibiting the fact that all electronic sites relax. This will *not* be so for case (b) [where the level width δ_L is given by $W(L)$] as shown below.

(b) *Levels with a length-dependent energy width* $W(L)$. We return to Eq. (6) and set $\delta_L=W(L)$ and $\delta_0=W_{\max}$. Inserting these relations into Eq. (8), we obtain

$$\begin{aligned}\bar{P}_{(\text{b})}(W)dW=\;&c_2(D/d_\phi)[\ln(W_{\max}/W)]^{(D/d_\phi)-1}\\&\times dW/W_{\max}\ ,\end{aligned} \tag{14}$$

where

$$c_2(\omega_0)=2^{D/d_\phi}N_{\text{fr}}(\omega_0)(l_{\omega_0})^D W_{\max}\ . \tag{15}$$

In this case,

$$\int_0^{W_{\max}}dW\,\bar{P}(W)=c_2(D/d_\phi)\Gamma(D/d_\phi)$$

does not diverge. Here, $\Gamma(\eta)$ is the gamma function. This means that, for the self-consistent case where the system energy width is the electronic relaxation rate itself, vibrational states far away from the electronic site do not contribute to the relaxation process. The total number of relaxing channels ($W \neq 0$) remains finite.

Inserting Eq. (14) into Eq. (10), we find the probability distribution for the largest W to equal

$$P_r(W)\,dW = c_2(D/d_\phi)[\ln(W_{\max}/W)]^{(D/d_\phi)-1}\exp\{-c_2(D/d_\phi)[\Gamma(D/d_\phi)-\Gamma(D/d_\phi,\ln(W_{\max}/W))]\}\,dW/W_{\max}\ , \tag{16}$$

where $\Gamma(\eta,z)$ is the incomplete gamma function, and the subscript r means relaxing. This notation is introduced because the probability density Eq. (16) is not normalized. One has

$$\int_0^{W_{\max}} dW\,P_r(W) = 1-\exp[-c_2(D/d_\phi)\Gamma(D/d_\phi)]\ , \tag{17}$$

which means that a fraction

$$\exp[-c_2(D/d_\phi)\Gamma(D/d_\phi)]$$

of the electronic states does not relax. This contribution to the probability density for the largest W is therefore

$$P_{\mathrm{nr}}(W)\,dW = \exp[-c_2(D/d_\phi)\Gamma(D/d_\phi)]\delta(W)\,dW\ , \tag{18}$$

where the subscript nr signifies nonrelaxing. These are sites for which the largest channel relaxation rate is zero.

The probability density for the largest W is the sum of Eqs. (16) and (18):

$$P_{(\mathrm{b})}(W)\,dW = P_r(W)\,dW + P_{\mathrm{nr}}(W)\,dW\ . \tag{19}$$

Thus, within this approximation one has two distinct populations. The reason for this behavior is clearly that δ_L decreases very fast (exponentially) with L while the number of states in a shell of radius L increases only to the power $D-1$ of L.

In general, the fracton (or electronic) state may have an intrinsic inverse lifetime less than $W_{\max}$. In such a case, δ_L will be given by $W(L)$ for distances less than a certain cutoff L_c. For L larger than L_c, the width $W(L)$ is smaller than the fracton intrinsic width, and δ_L will be independent of L. This situation is a simple combination of cases (a) and (b) treated above.

IV. TIME PROFILE AND AVERAGE RELAXATION RATE

We now use the probability density for the largest relaxation rate, $P(W)$, to calculate the time profile of the electronic state population and the average relaxation rate. The latter is relevant for cases of rapid cross relaxation. (Note that we have considered so far the probability density only for the largest electronic relaxation rate. The smaller rates could in principle sum to a value comparable to or larger than the largest rate. In fact, this is not the case, as discussed in the Appendix. Only logarithmic corrections are found.)

The time dependence for the occupation of the initial electronic state is given by the Laplace transform of the probability density $P(W)$:

$$P(t) = \int_0^{W_{\max}} dW\,\exp(-Wt)P(W)\ . \tag{20}$$

In case (a), using Eq. (13), we can write

$$P_{(\mathrm{a})}(t) = c_1\int_0^{\infty} Dz\,\exp\{-c_1 z - W_{\max}t\,\exp[-(z)^{d_\phi/D}]\}\ , \tag{21}$$

where we have substituted

$$z = [\ln(W_{\max}/W)]^{D/d_\phi}\ . \tag{22}$$

We carry out the z integration in Eq. (21) by the saddle-point method. The saddle point z_a obeys the equation

$$\tau_a = z_a^{[1-(d_\phi/D)]}\exp[(z_a)^{d_\phi/D}]\ , \tag{23}$$

$$\tau_a = (d_\phi/D)(W_{\max}t/c_1)\ . \tag{24}$$

In the large τ_a limit (long times) one has the iterative solution

$$z_a^{d_\phi/D} = \ln\tau_a - \ln[(\ln\tau_a)^{(D/d_\phi)-1}] - \cdots = \ln\left[\frac{\tau_a}{\left[\ln\left[\dfrac{\tau_a}{\left[\ln\left[\dfrac{\tau_a}{\cdots}\right]\right]^{(D/d_\phi)-1}}\right]\right]^{(D/d_\phi)-1}}\right]\ . \tag{25}$$

This form, a logarithmic generalization of a continued fraction, is convergent. Retaining only the leading order in Eq. (25) (neglecting logarithmic corrections in the exponent), we obtain from Eq. (21)

$$P_{(\mathrm{a})}(t) \sim [2\pi(D/d_\phi)c_1]^{1/2}(\ln\tau_a)^{(D-d_\phi)/2d\phi}\,\tau_a^{-c_1[\ln\tau_a]^{(D/d_\phi)-1}}\ , \tag{26}$$

where τ_a is given in Eq. (24). Equation (26) describes the long-time behavior of the population of the initial electronic state. It shows that the population decays faster than a power law but slower than exponential (or stretched exponential).

For case (b), use of Eqs. (16), (18), and (19) in Eq. (20) yields

$$P_{(b)}(t)=[\exp(-\alpha c_2)]\left[1+c_2\int_0^\infty dz\exp\{-(z)^{d_\phi/D}-W_{\max}t\exp[(-z)^{d_\phi/D}]+c_2(D/d_\phi)\Gamma(D/d_\phi,(z)^{d_\phi/D})\}\right], \tag{27}$$

where we have used the substitution given by Eq. (22). In Eq. (27), $\alpha=(D/d_\phi)\Gamma(D/d_\phi)$ is a numerical constant. The first term in the large parentheses represents the contribution to $P_{(b)}(t)$ of those electronic states which are nonrelaxing [Eq. (18)]. The saddle point z_b of the z integration in Eq. (27) obeys the equation

$$\tau_b=\exp[(z_b)^{d_\phi/D}]+(D/d_\phi)c_2(z_b)^{1-(d_\phi/D)}, \tag{28a}$$

where we have defined

$$\tau_b=W_{\max}t\ . \tag{28b}$$

In the large τ_b limit, the saddle point z_b has the form

$$(z_b)^{d_\phi/D}=\ln(\tau_b-(D/d_\phi)c_2\{\ln[\tau_b-(D/d_\phi)c_2[\ln(\tau_b-\cdots)]^{(D/d_\phi)-1}]\}^{(D/d_\phi)-1})\ . \tag{29}$$

We again neglect logarithmic corrections, keeping only the leading-order term in Eq. (29). Then, Eq. (27) yields

$$P_{(b)}(t)\sim\exp(-\alpha c_2)+(D/d_\phi)c_2\sqrt{2\pi}\exp[-(\alpha c_2+1)](1/\tau_b)(\ln\tau_b)^{(D/d_\phi)-1}, \tag{30}$$

where τ_b is defined by Eq. (28). One sees that the population decay in case (b) is slower than in case (a), and is closer to a power law. At very long times the initial-state electronic population approaches a constant value, $\exp(-\alpha c_2)$, just the fraction of nonrelaxing electronic sites.

Another interesting feature of the relaxation rate probability density is its average value. This will be important when the spin-spin interaction is in excess of $W_{\max}$. Under these conditions of strong cross relaxation, all spins relax exponentially in time at an average relaxation rate,

$$\langle W\rangle=\int_0^{W_{\max}}dW\,WP(W)\ . \tag{31}$$

For case (a), from Eq. (13),

$$\langle W_{(a)}\rangle=W_{\max}^{(a)}c_1\int_0^\infty dz\exp\{-[c_1z+(z)^{d_\phi/D}]\}, \tag{32}$$

where we have used the substitution dictated by Eq. (22). For small values of c_1 [Eq. (12)] the integral in Eq. (32) approaches $(D/d_\phi)\Gamma(D/d_\phi)$, so that the average relaxation rate $\langle W_{(a)}\rangle$ is of order $W_{\max}^{(a)}c_1$. For case (b), from Eqs. (16), (18), and (19),

$$\langle W_{(b)}\rangle=W_{\max}^{(b)}c_2\int_0^\infty dz\exp\{-2(z)^{d_\phi/D}-c_2(D/d_\phi)[\Gamma(D/d_\phi)-\Gamma((D/d_\phi),(z)^{d_\phi/D})]\}\ . \tag{33}$$

In the small c_2 [Eq. (15)] limit, the integral in Eq. (33) becomes $(2^{-D/d_\phi})(D/d_\phi)\Gamma(D/d_\phi)$. Summarizing, we have

$$\langle W_{(a)}\rangle\sim W_{\max}^{(a)}c_1\equiv W_{\max}^{(a)}N_{\mathrm{fr}}(\omega_0)(l_{\omega_0})^D\delta\ , \tag{34a}$$

$$\langle W_{(b)}\rangle\sim W_{\max}^{(b)}c_2(2)^{-D/d_\phi}\equiv(W_{\max}^{(b)})^2N_{\mathrm{fr}}(\omega_0)(l_{\omega_0})^D\ . \tag{34b}$$

Comparing Eq. (5) with Eq. (6), one sees that, in case (a)

$$W_{\max}^{(a)}\sim\omega_0^{2q-1}(l_{\omega_0})^{-D}\coth(\beta\omega_0/2)/\delta\ , \tag{35a}$$

while in the self-consistent case (b),

$$W_{\max}^{(b)}\sim[\omega_0^{2q-1}(l_{\omega_0})^{-D}\coth(\beta\omega_0/2)]^{1/2}\ . \tag{35b}$$

This should be substituted into Eqs. (34) to obtain the explicit form of $\langle W_{(a)}\rangle$ and $\langle W_{(b)}\rangle$.

The average relaxation rate can also be calculated directly by averaging the golden-rule expression for the transition rate. We integrate the golden-rule expression over all fracton modes to obtain [see Eq. (5)]

$$\langle W\rangle\sim N_{\mathrm{fr}}(\omega_0)\omega_0^{2q-1}\coth(\beta\omega_0/2)\ , \tag{36}$$

where we have used the fact that the wave functions ϕ_α [Eq. (3)] are normalized. Comparing this with the result of the substitution of Eq. (35) in Eq. (34), one notes that all three expressions have the same functional form

$$\langle W_{(a)}\rangle\sim W_{(b)}\rangle\sim\langle W\rangle\ . \tag{37}$$

We note that $\langle W\rangle$ is an average of the total relaxation rate, while $\langle W_{(a)}\rangle$ and $\langle W_{(b)}\rangle$ are averages of the largest single-site rate. Thus there must be numerical factors which cause these quantities to differ. These factors arise from the effect of relaxation rates smaller than the largest. Their effect upon the probability density for the relaxation rate, and the time decay profile, are explicitly calculated in the Appendix.

The dependence of the average relaxation rate upon the magnitude of the energy transfer ω_0 is

$$\langle W\rangle\sim\begin{cases}\omega_0^{2q+\bar{\bar{d}}-2}, & \beta\omega_0\gg1\\ \omega_0^{2q+\bar{\bar{d}}-3}/\beta, & \beta\omega_0\ll1\ .\end{cases} \tag{38}$$

It is interesting to investigate the reasons for the difference in the ω_0 dependence of $W_{\max}$ for the cases (a) and (b) [as exhibited by Eqs. (35)]. Let us assume that the average relaxation rate consists of a fraction p of electronic levels for which the relaxation is fast, and a fraction $(1-p)$ for which the relaxation is much slower. Then

$$\langle W \rangle = p\{W\}_{\text{fast}} + (1-p)\{W\}_{\text{slow}} \; . \tag{39}$$

To estimate p, we note that electronic states with a suitable fracton within a distance l_{ω_0} will relax rapidly. The number of such strongly relaxing levels is $N_{\text{fr}}(\omega_0) l_{\omega_0}\delta$. If this is small, this also represents the fraction of electronic states which relax rapidly. Thus,

$$p \approx N_{\text{fr}}(\omega_0) l_{\omega_0}\delta \; , \tag{40}$$

and the fast relaxation rate $\{W\}_{\text{fast}}$ is $W_{\max}$. Other sites relax slowly. Neglect of $\{W\}_{\text{slow}}$ in the average gives

$$\{W\}_{\text{fast}} = W_{\max} = \langle W \rangle / [N_{\text{fr}}(\omega_0)(l_{\omega_0})^D \delta] \; . \tag{41}$$

One sees that Eq. (41) leads directly to $W_{\max}$ of case (a), Eq. (35a). For case (b), $W_{\max}$ is just δ. Therefore, from Eq. (41),

$$W_{\max} = [\langle W \rangle / N_{\text{fr}}(\omega_0)(l_{\omega_0})^D]^{1/2} \; ,$$

which is Eq. (35b).

This argument also clarifies another point which is crucial for the manner by which our calculation was performed, and which tends to be obscured by the algebra. We have assumed that $p \approx c_1$ [see Eqs. (12) and (40)] is very small. It is then sufficient to evaluate the probability for the largest single relaxation rate channel available at a given site. Other channels will have much slower relaxation rates, and consequently will play a relatively minor role overall (for details, see the Appendix). It is evident, however, that p, as defined in Eq. (40), can become large should l_{ω_0} be sufficiently large. Most electronic states would then have a large number ($\sim p$) of parallel relaxation channels available, each contributing $\approx W_{\max}$ to the total rate. The density of sites which would not relax at this rate would be small [$\sim \exp(-p)$].

One should note that, for either limit (small or large p), the average $\langle W \rangle$ does not depend upon δ and l_ω. However, the statistical distribution depends strongly upon p, becoming much narrower when p is large.

V. COMPARISON OF THE CONTRIBUTION TO THE RELAXATION TIME OF FRACTONS AND LOCALIZED PHONONS

Localized phonon modes describe vibrations in a sufficiently disordered Euclidean network. Setting $\bar{\bar{d}} = D = d$ and $d_\phi = 1$ in the expressions above transforms the fracton density of states into the usual phonon density of states. Secondly, because we shall take the localized phonons to obey the usual linear dispersion law, the spatial derivative of the wave function is proportional to the energy. Hence, the energy index q appearing in the golden-rule expression for the relaxation rate [see Eq. (5)] is equal to unity. Thirdly, because we assume the localization length ξ for localized phonons is a constant independent of the mode energy, we replace l_{ω_0} by ξ in the expressions above.

As a consequence of these modifications, the relaxation of localized electronic states by localized phonons differs from that induced by fractons in two respects. The first aspect is the numerical value of the power law of $\ln(W_{\max}/W)$. This fact governs the probability distributions and consequently the time profiles. In three dimensions, for example, the time profile for case (a) becomes [from Eq. (26)]

$$P_{(\mathrm{a})}(t) \sim (\ln\tau_a)\tau_a^{-c_1(\ln\tau_a)^2} \; , \tag{42a}$$

and that for case (b) [from Eq. (30)],

$$P_{(\mathrm{b})}(t) \sim \tau_b^{-1}(\ln\tau_b)^2 \; . \tag{42b}$$

The second aspect pertains to the time scale, as derived from the energy dependence of $W_{\max}$ and the coefficients c_1 and c_2. Form Eqs. (35) we found for fracton-induced relaxation

$$W_{\max} = \begin{cases} \omega_0^{2q-1+\bar{\bar{d}}}, & \text{case (a)} \\ (\omega_0^{2q-1+\bar{\bar{d}}})^{1/2}, & \text{case (b)} \end{cases} \tag{43}$$

at zero temperature, where we have used Eq. (4). Using the transformations described above, the analogous results for phonon relaxation are

$$W_{\max} \sim \begin{cases} \omega_0 \xi^{-d}, & \text{case (a)} \\ \omega_0^{1/2} \xi^{-d/2}, & \text{case (b)} \; . \end{cases} \tag{44}$$

The exponent in Eq. (43), $2q-1+\bar{\bar{d}}$, is larger than zero for most physical systems. As a consequence, $W_{\max}$ increases with energy in both situations. However, the coefficients c_1 and c_2 [which govern the time profiles—see Eqs. (24), (26), (28), and (30)] depend differently on energy for fractons and localized phonons. Both c_1 and c_2 are proportional to the product of the vibrational density of states with the localization volume [see Eqs. (12) and (15)]. For fractons, this combination is inversely proportional to ω_0. The same quantity is proportional to ω_0^{d-1} for localized phonons. Thus, the principal difference between fracton and localized phonon relaxation lies in the energy dependence of c_1 and c_2. This is directly related to the energy dependence of the localization length l_{ω_0} of the fractons, as compared to our assumption of an energy-independent phonon localization length ξ.

VI. CONCLUSIONS

We have shown how localization of vibrational excitations can profoundly affect the relaxation of localized electronic states. We have calculated the distribution of relaxation rates for two limiting conditions: the combined energy widths of the electronic and vibrational states independent of the distance between them, and the combined energy widths equal to the relaxation rate itself. The former should be relevant when, for example, the vibrational energy width, because of anharmonicity, exceeds the relaxation rate. The latter is relevant when the reverse is true. Clearly, there are other limits: the anharmonic width of the fracton states is intermediate to the relaxation rates; cross relaxation introduces an electronic energy width intermediate to the relaxation rates.

We have used the distributions of relaxation rates we have derived to calculate the time dependence of the occupation of the initial electronic states. We have found remarkable differences from exponential. For a combined vibrational and electronic width independent of distance between them, we find a time dependence which decays faster than any power law, but slower than exponential (or stretched exponential). For the opposite extreme, when the combined width is taken equal to the relaxation rate itself, the electronic states split into two groups: those which relax as a power law in time, and those which do not undergo relaxation at all (via the one-fracton mechanism).

When rapid cross relaxation is present, one can speak of an average relaxation rate for the entire electronic system. This is calculated in Sec. IV for both limits considered above. A direct "golden-rule" calculation of the average relaxation rate is shown to have the same analytic form as these averages, the numerical differences arising from the effect of relaxation rates smaller than the largest.

The use of these calculations should shed light upon electronic relaxation processes in disordered materials. Nonexponential decays are observed extensively in the literature on electronic relaxation in amorphous hosts. Our results can be used as an explicit means of comparison, or "in reverse" as an indication of the character of the vibrational spectrum in such materials. Examples are amorphous semiconductors where photoexcited electron-hole pairs below the conduction edge decay faster than power law, but slower than exponential with time.[18] Other examples are electronic centers in glasses. The nonradiative relaxation rate should follow the time profiles calculated in this paper when the splitting between electronic states is less than the fracton Debye energy.[7]

Clearly, higher-order vibrational processes may be important at high temperatures or when the change in electronic energy exceeds the fracton Debye energy. In a separate paper, we calculate the two-fracton electronic relaxation rate for localized electronic centers.[9,10] Here too we find dramatic differences from that calculated with extended vibrational states, including stretched exponential and time decays of the form of Eq. (26). For two-fracton relaxation processes, the explicit temperature dependence of the average relaxation rate differs from that calculated for extended vibrational states, in contrast to the one-fracton relaxation process treated here (see the discussion in Sec. IV).

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APPENDIX: CORRECTIONS TO THE LARGEST RELAXATION PROBABILITY DENSITY

We have derived in Sec. III the probability density $P(W)$ that W is the largest relaxation rate of a given electronic site. We have then used $P(W)$ to find the time profile for the electronic state occupation, and for the average relaxation rate. We shall now consider the contributions coming from relaxation rates *smaller* than the largest, i.e., from fracton states further away from the electronic site.

The sum of the relaxation rates up to a certain rate W_t is

$$\overline{W}(W_t)=\int_0^{W_t} dW_1\, W_1\overline{P}(W_1)\;, \tag{A1}$$

where $\overline{P}(W)$ is the probability density for W, Eq. (8). The effective relaxation rate $\widetilde{W}$ not larger than W_t is then

$$\widetilde{W}=W_t+\overline{W}(W_t)\;. \tag{A2}$$

inverting this equation to obtain $W_t(\widetilde{W})$, we find that the probability density $\widetilde{P}(\widetilde{W})$ for the largest $\widetilde{W}$ is

$$\widetilde{P}(\widetilde{W})=P(W_t(\widetilde{W}))\left[\exp-\int_{W_t(\widetilde{W})}^{W_{\max}} dW_1\,P(W_1)\right] \times dW_t(\widetilde{W})/d\widetilde{W}\;. \tag{A3}$$

$\widetilde{P}(\widetilde{W})$ is the probability density for $\widetilde{W}$ values in the range $0\le\widetilde{W}\le\widetilde{W}_{\max}$, where

$$\widetilde{W}_{\max}=W_{\max}+\overline{W}(W_{\max})\;. \tag{A4}$$

It is clear that when the contribution of the relaxation rates smaller than W_t is neglected, $\widetilde{W}=W_t$ and $\widetilde{P}(\widetilde{W})$ is just the probability density $P(W)$ calculated in Sec. III [Eq. (10)]. The procedure outlined in Eqs. (A1)—(A4) allows us to calculate corrections to $P(W)$ arising from the sum of contributions smaller than the largest experienced at a given electronic site.

1. Constant energy width

Inserting Eq. (11) for $\overline{P}_{(a)}$ into Eq. (A1), we find from Eq. (A2)

$$\widetilde{W}=W_t+c_1(D/d_\phi)W_{\max}\Gamma((D/d_\phi),\ln(W_{\max}/W_t))\;, \tag{A5}$$

and from Eq. (A4),

$$\widetilde{W}_{\max}=W_{\max}[1+c_1(D/d_\phi)\Gamma(D/d_\phi)]\;, \tag{A6}$$

where c_1 is given by Eq. (12). The probability density $\widetilde{P}(\widetilde{W})$, from Eq. (A3), is

$$\widetilde{P}_{(\mathrm{a})}(\widetilde{W})=c_1(D/d\phi)[W_t(\widetilde{W})]^{-1}\{\ln[W_{\max}/W_t(\widetilde{W})]\}^{D/d_\phi-1}\frac{\exp(-c_1\{\ln[W_{\max}/W_t(\widetilde{W})]\}^{D/d_\phi})}{1+c_1(D/d_\phi)\{\ln[W_{\max}/W_t(\widetilde{W})]\}^{D/d_\phi-1}}\ , \tag{A7}$$

where $W_t(\widetilde{W})$ is the solution of Eq. (A5). We find the limiting behaviors of the probability density $\widetilde{P}_{(\mathrm{a})}(\widetilde{W})$ by using expansions of the incomplete gamma function. We have

$$W_{\max}-W_t\sim(\widetilde{W}_{\max}-\widetilde{W})\{1-c_1[(\widetilde{W}_{\max}-\widetilde{W})/W_{\max}]^{D/d_\phi-1}\}\ , \tag{A8a}$$

when $W_t/W_{\max}\sim 1$, and

$$W_{\max}/W_t\sim(W_{\max}/\widetilde{W})\{1+c_1(D/d_\phi)[\ln(W_{\max}/\widetilde{W})]^{D/d_\phi-1}\}\ , \tag{A8b}$$

when $W_t/W_{\max}\ll 1$. Thus, in the limit of small relaxation rate $\widetilde{W}$, the probability $\widetilde{P}_{(\mathrm{a})}$ contains logarithmic corrections as compared to the probability density $P_{(\mathrm{a})}$ [Eq. (13)], which are small when c_1 is small [see the discussion after Eq. (41)].

Turning now to the Laplace transform of $\widetilde{P}_{(\mathrm{a})}$, we find

$$\begin{aligned}\widetilde{P}_{(\mathrm{a})}(t)&=\int_0^{\widetilde{W}_{\max}}d\widetilde{W}\exp(-\widetilde{W}t)\widetilde{P}_{(\mathrm{a})}(\widetilde{W})\\&=c_1\int_0^\infty dz\exp\{-c_1z-W_{\max}t[\exp[-(z)^{d_\phi/D}]+c_1(D/d_\phi)\Gamma((D/d_\phi),(z)^{d_\phi/D})]\}\ ,\end{aligned} \tag{A9}$$

where we have used Eqs. (A5)—(A7), and the substitution dictated by Eq. (22). Carrying out the z integration by the method of saddle points yields

$$\widetilde{P}_{(\mathrm{a})}(t)\sim[2\pi(D/d_\phi)c_1]^{1/2}(\ln\widetilde{\tau}_a)^{(D-d_\phi)/2d_\phi}(\widetilde{\tau}_a)^{-c_1(\ln\widetilde{\tau}_a)^{D/d_\phi-1}}\ , \tag{A10}$$

where

$$\begin{aligned}\widetilde{\tau}_a&=W_{\max}t+\tau_a(\ln W_{\max}t)^{1-D/d_\phi}\ ,\\\tau_a&=(d_\phi/D)W_{\max}t/c_1\ .\end{aligned} \tag{A11}$$

We see that $\widetilde{P}_{(\mathrm{a})}(t)$ has the same functional form as $P_{(\mathrm{a})}(t)$ [Eq. (26)] but with a different time scale $\widetilde{\tau}_a$, which includes logarithmic corrections to τ_a.

2. Length-dependent energy width

Inserting Eq. (14) for $P_{(\mathrm{b})}$ into Eq. (A1), Eq. (A2) takes the form

$$\widetilde{W}=W_t+c_2(D/d_\phi)(1/2)^{D/d_\phi}W_{\max}\Gamma((D/d_\phi),2\ln(W_{\max}/W_t))\ , \tag{A12}$$

and the maximum relaxation rate seen by a given site becomes [see Eq. (A4)]

$$\widetilde{W}_{\max}=W_{\max}[1+c_2(D/d_\phi)(1/2)^{D/d_\phi}\Gamma(D/d_\phi)]\ , \tag{A13}$$

where c_2 is given in Eq. (15). The probability density $\widetilde{P}_{(\mathrm{b})}$ is [from Eq. (A3)]

$$\begin{aligned}\widetilde{P}_{(\mathrm{b})}(\widetilde{W})=c_2(D/d_\phi)W_{\max}^{-1}&\{\ln[W_{\max}/W_t(\widetilde{W})]\}^{D/d_\phi-1}\\&\times(1+c_2(D/d_\phi)[W_t(\widetilde{W})/W_{\max}]\{\ln[W_{\max}/W_t(\widetilde{W})]\}^{D/d_\phi-1})^{-1}\\&\times\exp[-c_2(D/d_\phi)\{\Gamma(D/d_\phi)-\Gamma((D/d_\phi),\ln[W_{\max}/W_t(\widetilde{W})])\}]\end{aligned} \tag{A14}$$

and $W_t(\widetilde{W})$ is the solution of Eq. (A12). The limiting behaviors of the solutions are

$$W_{\max}-W_t\sim(\widetilde{W}_{\max}-\widetilde{W})\{1-c_2[(\widetilde{W}_{\max}-\widetilde{W})/W_{\max}]^{D/d_\phi-1}\}\ , \tag{A15a}$$

when $W_t/W_{\max}\sim 1$, and

$$W_{\max}/W_t\sim(W_{\max}/\widetilde{W})\{1+c_2(D/2d_\phi)(\widetilde{W}/W_{\max})[\ln(W_{\max}/\widetilde{W})]^{D/d_\phi-1}\}\ , \tag{A15b}$$

when $W_t/W_{\max}\ll 1$. As in the case of constant energy width, only logarithmic corrections are found in the small relaxation rate limit, which are small when c_2 is small.

The Laplace transform of $\widetilde{P}_b$ is

$$\begin{aligned}\widetilde{P}_{(\mathrm{b})}(t) &= \int_0^{\widetilde{W}_{\max}} d\widetilde{W}\exp(-\widetilde{W}t)\widetilde{P}_{(\mathrm{b})}(\widetilde{W}) \\ &= c_2\int_0^{\infty} dz\exp\{-c_2(D/d_\phi)[\Gamma(D/d_\phi)-\Gamma((D/d_\phi),(z)^{d_\phi/D})]-(z)^{d_\phi/D} \\ &\qquad - W_{\max}t[\exp[-(z)^{d_\phi/D}]+c_2(1/2)^{D/d_\phi}(D/d_\phi)\Gamma((D/d_\phi),2(z)^{d_\phi/D})]\}\ ,\end{aligned} \tag{A16}$$

where we have used the substitution dictated by Eq. (22). A saddle-point integration yields

$$\widetilde{P}_{(\mathrm{b})}(t)\sim(D/d_\phi)c_2\sqrt{2\pi}\exp[-(\alpha c_2+1)](1/\tau_b)(\ln\tau_b)^{(D/d_\phi)-1}[1+c_2(D/d_\phi)(1/\tau_b)(\ln\tau_b)^{(D/d_\phi)-1}]^{-1/2}\ , \tag{A17}$$

where $\tau_a=W_{\max}t$. Comparing Eq. (A17) with the second member of $P_{(\mathrm{b})}(t)$ [see Eq. (30)], we see that Eq. (A17) includes only a small correction to our previous result. In this case, the time scale does not change.

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