# DYNAMICAL PROCESSES IN DISORDERED SYSTEMS

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## ABSTRACT

We discuss the effect of disorder on dynamical processes in solids. In particular, we treat donor (to acceptor) decay, excitation diffusion, trapping and optical line shapes in disordered systems. The modelling of disorder with fractals is discussed.

## I. INTRODUCTION

The presence of disorder in solids has a substantial effect on the energy levels (both electronic and vibrational) and on the dynamics of particles and excitations travelling through the solid. An enormous amount of effort has gone into studying these effects, both experimentally and theoretically. In this article, I will necessarily be forced to restrict my comments to a small subset of the possible interesting topics. I will in fact discuss issues which arise in the optical spectroscopy of such solids; however these will exhibit the interesting problems which occur when disorder is present in a solid. The plan of the article is to begin with the dynamics of the transfer of excitation from a single excited donor to a collection of randomly arranged acceptors. The disorder gives rise to a dramatic change in the time dependence which is highly dependent on density (of acceptors) and on the dimensionality of the space. Next, we will examine the transport of an excitation among similar molecules randomly arranged on a lattice. We will discuss the time dependence and the diffusion coefficient of this transport and their dependence on density and dimensionality. The trapping of excitations during this diffusion process will also be discussed. We will then go on to examine the effect of disorder on the optical line shapes of molecules in solids. Here we will discuss the ways of dealing with the weak disorder case and the strong disorder case.

After these detailed studies, we will go on to discuss the modelling of disorder fractals. After an introduction to this concept, we will discuss the effects of fractal structure on the dynamic problems we discussed above.

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## II. FÖRSTER TRANSFER [1-10]

The simplest process we can imagine which exhibits the effects of disorder is that of excitation transfer from an excited molecule to a large number of acceptor molecules arranged in space in some way. The time dependent probability of finding the excitation on the $\alpha$th donor molecule is

$$\frac{dp_\alpha(t)}{dt} = -\sum_i W_{i\alpha}\, p_\alpha(t) - \frac{1}{\tau}\, p_\alpha(t) \tag{1}$$

where $W_{i\alpha}$ is the rate of energy transfer from the donor to the ith acceptor at position $r_i$ and $\tau$ is the lifetime of the excitation in the absence of acceptors. We take the donor position to be at $r_\alpha$ and assume that the donors are very far apart, so they do not interact with one another. In addition, we assume that $W_{i\alpha}$ is a function of $\mathbf{r}_i - \mathbf{r}_\alpha$. In fact, we normally assume that it is a function of $|\mathbf{r}_i - \mathbf{r}_\alpha|$ only, although although some concern has been raised about this. The solution to Eq. (1) is immediate:

$$p_\alpha(t) = e^{-\left(\sum_i W_{i\alpha}\right)t}\, e^{-t/\tau} = \left[\prod_i e^{-W_{i\alpha}t}\right] e^{-t/\tau} \tag{2}$$

The experimenter measures the fluorescence decay of the donor molecules and infers the "extra" decay due to the donor-acceptor transfer. If the acceptors were arranged in exactly the same manner around each donor, then the problem is done and the donor-acceptor transfer has changed the exponential decay rate from $1/\tau$ to $1/\tau + \sum W_{i\alpha}$. However, the assumption of order is incorrect: each donor sees a different arrangement of acceptors, so the experimentally determined variable is the average of $P_\alpha(t)$ over all possible arrangements:

$$\langle p(t)\rangle = \left\langle \prod_i e^{-W_{i\alpha}t} \right\rangle e^{-t/\tau} \equiv \Phi(t)\, e^{-t/\tau} \tag{3}$$

where we have assumed that the lifetime in the absence of acceptors is independent of donor position in the solid. In order to carry out this configurational average, we can assume that the acceptors are arranged on a lattice and that the probability of any lattice site being occupied by an acceptor is p and that it is unoccupied is (1-p). Then, we have for uncorrelated sites,

$$\Phi(t) = \prod_i \left[(1-p) + p\, e^{-W_{i\alpha}t}\right] \tag{4}$$

where the product is now over all lattice sites. We can rewrite this as

$$\Phi(t) = \exp\left[\sum_i \log\{1-p + p e^{-W_{i\alpha}t}\}\right] \tag{5a}$$

$$\simeq \exp -\left[p\sum_i \{1 - e^{-W_{i\alpha}t}\}\right] \tag{5b}$$

for small p. Finally we can convert the sum over lattice sites to an integral over the volume. Defining concentration of acceptors by

$$c = p(N/V) \tag{6}$$

we find

$$\Phi(t) = \exp[- c \int_{R_{min}}^{R_{max}} d\mathbf{r} \; \{1 - e^{-tW(r)}\}] \tag{7}$$

Here we have replaced $W_{i\alpha}$ by $W(|\mathbf{r}_i - \mathbf{r}| = W(r)$ and placed the donor molecule at the origin. If we now assume that $W(r)$ has a multipolar form: $W(r) = \alpha/r^s$ ($s = 6$ is the Förster dipole-dipole transfer rate) and that the transfer takes place in a space of dimension $d$, we find (with spherical volume element $d\mathbf{r}$ is replaced by $r^{d-1} A_d dr$ since the integrand is independent of angle)

$$\Phi(t) = \exp\{-cA_d \int_{R_{min}}^{R_{max}} dr \; r^{d-1}[1-e^{-\alpha t/r^s}]\} \tag{8}$$

The upper limit, $R_{max}$, is the dimension of the region containing acceptors in which acceptors interact with the donor. The integral can be transformed into a $\Gamma$ function for $\alpha t/R^s{}_{max} \ll 1$ (i.e. for times short compared to the inverse rate to the farthest donor) and $\alpha t/R^s{}_{min} \gg 1$ (times long compared to the inverse rate to the nearest neighbor molecule.)

$$\Phi(t) = \exp\{-A_d \overset{\frac{c}{d}}{\underset{\wedge}{}}(\alpha t)^{d/s} \; \Gamma(1 - \tfrac{d}{s})\} \tag{9}$$

So here we see our first example of a strong effect of disorder: the exponential decay law has been modified to a decay <u>nonlinear</u> in time. The usual case of $d = 3$, $s = 6$ yields a $t^{1/2}$ which has been known since Förster's pioneering work. Note that a crucial assumption in the above was to replace the actual distribution of acceptor molecules by an average distribution proportional to $c d\mathbf{r}$.

The form of the decay of $\langle p(t) \rangle$ is an example of a "stretched exponential":

$$e^{-(t/t_o)^\beta} \quad . \tag{10}$$

In the Förster case $\beta = 1/2$, but as we see from the above $\beta = d/s$ is possible for $s > d + 1$.

If instead of a multipole transfer rate, an exponential $w(r) = W_o e^{-\gamma r}$ (exchange transfer) were chosen, then we find

$$\Phi(t) = \exp - \{A_d \frac{C}{\gamma^d} g_d(W_o t)\} \tag{11}$$

where $g_d(Wt)$ are functions introduced by Inokuti and Hirayama [2] and discussed extensively by Blumen [7,8]. In the limit of long times (but still short compared to $W_o^{-1} e^{\gamma R_{max}}$) these authors find

$$g_d(x) \sim \ell n^d(W_o t) \tag{12}$$

This decay is slower than the stretched exponential form found for multipolar transfer. This is sometimes called an exponential log decay.

We should point out for completeness, that often the experimentally relevant parameter is the branching ratio, i.e. the ratio of the radiative rate to the total rate. From Eq. (3), we can write this as

$$\eta = \left\langle \frac{\tau^{-1}}{\tau^{-1} + \sum_i W_{i\alpha}} \right\rangle \tag{13}$$

which is just $\tau^{-1}$ multiplied by the Laplace transform of $\Phi(t)$ evaluated at $\tau^{-1}$:

$$\eta = \tau^{-1}\tilde{\Phi}(u)\Big|_{u = \tau^{-1}} \tag{14}$$

where $\tilde{\Phi}(u)$ is

$$\tilde{\Phi}(u) = \int_0^{\infty} e^{-ut}\Phi(t)dt \tag{15}$$

As a final point in our present discussion of donor-acceptor transfer, we can ask what would happen if the acceptors were arranged in a non-isotropic manner. A simple example will suffice: suppose the acceptors are arranged in a cylinder of radius $R_1$ and length $R_2 << R_1$. Assume multipolar decay $W(r) = \alpha/r^s$, then for times such that $\alpha t/R_2{}^s << 1$, the decay is three-dimensional. However, for times such that $\alpha t/R_2{}^s >> 1$ (but $\alpha t/R_1{}^s << 1$) the decay will resemble the 2-dimensional rate. This is an example of the effect of restricted geometries.

## III. EXCITATION OR PARTICLE TRANSPORT [11-23]

### III.A. Formal Manipulations

Another important process which is strongly affected by disorder is the transport of excitations in a solid. We will only be concerned with incoherent transport, that transport which can be described by the master equation. The simplest physical situation is to assume that many donors are arranged at random throughout the solid. The excitation is placed on one donor initially and the probability of finding the excitation on any donor, say the jth, at time t is $p_j(t)$. The equation of motion for $p_n(t)$ is

$$\dot{p}_n(t) = \sum_{\cancel{1}\,n} W_{nm}p_m(t) - \sum_{\cancel{1}\,n} W_{mn}p_n(t) - p_n(t)\tau^{-1} \tag{16}$$

The first term on the right represents the rate of transfer to the nth donor from the other donors; the second term is the rate of transfer from the nth donor. (If we assume that the lifetime of the donors, $\tau$, is independent of n, we can eliminate the last term by writing $p_n(t) = P_n(t)e^{-t/\tau}$. This is so straightforward we will merely drop the lifetime term altogether and, if needed, put it back later). For simplicity, we now take $W_{ji} = W_{ij}$.

For an ordered system, say a crystal, Eq. ~~(8)~~ (16) can be solved by assuming periodic boundary conditions and writing

$$p(k,t) = \frac{1}{N}\sum_n e^{i\underset{\sim}{k}\cdot\underset{\sim}{R}_n} P_n(t) \quad . \tag{17}$$

Then

$$\dot{p}(k,t) = -[W(\underset{\sim}{0}) - W(\underset{\sim}{k})]p(k,t)$$

or (18)

$$p(k,t) = \frac{1}{N} \exp\{[-W(\underset{\sim}{0}) + W(\underset{\sim}{k})]t\} \tag{19}$$

where we have assumed the excitation was originally at the origin and we have defined

$$W(\underset{\sim}{k}) \equiv \sum_{j} e^{i\underset{\sim}{k}\cdot(\underset{\sim}{r}_j - r_i)} W_{ji} \tag{20}$$

Thus the probability of finding the excitation on donor n is

$$p_n(t) = \frac{1}{N} \sum_{k} \exp\{[-W(\underset{\sim}{0}) + W(\underset{\sim}{k})]t\}\, e^{ik\cdot R_n} \tag{21}$$

At very ~~low~~ short times,

$$p_o(t) = e^{-tW(\underset{\sim}{0})} \tag{22}$$

and at along times we find

$$p_o(t) \sim t^{-d/2} \tag{23}$$

(d again the dimension of the system). We can calculate the mean square displacement of the excitation (initially at the origin)

$$\langle R^2(t)\rangle = \sum_{n} |\underset{\sim}{R}_n - \underset{\sim}{R}_o|^2\, p_n(t) = 2d\, Dt \tag{24}$$

with

$$D = \frac{1}{2d} \sum_{\cancel{j}\, n} W_{nm}\, |\underset{\sim}{R}_n - \underset{\sim}{R}_m|^2 \tag{25}$$

Thus for regular lattices, the transport of an excitation is diffusive at all times. Note however that the probability of being at the origin, $p_o(t)$, has a more complicated time dependence.

When disorder is present, the time dependence of the mean square displacement is more complex than Eq. (24). A number of different approaches have been taken for this problem. Here we will try to show the connections among some of these.

Consider a partially occupied lattice for which each site can be occupied by a molecule capable of carrying the excitation with probability p. Then the equation of motion for the probabilities of finding the excitation at one of the occupied sites is once again the master equation.

$$\dot{p}_n(t) = \sum_{m\neq n} W_{nm} p_m(t) - \sum_{m\neq n} W_{mn} p_n(t) \tag{26}$$

Note that probability is conserved so that $\Sigma\dot{p}_n(t) = 0$. An average over all possible starting points for the excitation for one configuration is the same as an average over all possible configurations of occupied sites on the lattice with the excitation starting at the origin. Eq. (26) can be formally solved by writing it in vector form

$$\dot{\underset{\sim}{p}}(t) = \underline{\underline{V}}p(t) \tag{27}$$

with

$$V_{nm} = (1-\delta_{nm})W_{nm} - \delta_{nm}\sum_{q\neq n} W_{qn}$$

Then

$$\underset{\sim}{p}(t) = (\exp t\underline{\underline{V}})\cdot\underset{\sim}{p}(0)$$

and, after configurational averaging,

$$\langle p_n(t)\rangle = \sum_m \langle e^{t\underline{\underline{V}}}\rangle_{no}$$

where we have now assumed the excitation began on the n = 0 siute. By Laplace transforming we find

$$\langle \hat{p}_n(u)\rangle = \langle (u\underline{\underline{I}} - \underline{\underline{V}})^{-1}\rangle_{no}$$

Using a projection operator formalism [18], we can rewrite this formal as

$$\langle \hat{p}_n(u)\rangle = [u\underline{\underline{I}} - \underline{\underline{M}}(u)]^{-1}_{no}$$

where M(u) is a self-energy matrix. In the time domain, this can be r written

$$\langle \dot{p}_n(t)\rangle = \int_0^t d\tau\{\sum_{\ell\neq n} M_{n\ell}(t-\tau)\langle p_\ell(\tau)\rangle + M_{nn}(t-\tau)\langle p_n(\tau)\rangle\}$$

Since probability is conserved

$$\sum_{\ell\neq n} M_{n\ell}(t-\tau) = - M_{nn}(t-\tau) \tag{34}$$

so that the final equation can be written in a form reminiscent of the original master equation, in which the time <u>independent</u> rates have bee replaced by time <u>dependent</u> kernels: this is the generalized master equ tion:

$$\langle \dot{p}_n(t)\rangle = \int_0^t d\tau\{\sum_{\ell\neq n} M_{n\ell}(t-\tau)\langle p_\ell(\tau)\rangle - \sum_{\ell\neq n} M_{\ell n}(t-\tau)\langle p_n(\tau)\rangle\} \tag{35}$$

or in Laplace transform

$$u\langle \hat{p}_n(t)\rangle - \langle p_n(0)\rangle = \sum_{\ell\neq n}\{\hat{M}_{n\ell}(u)\langle \hat{p}_\ell(u)\rangle - \hat{M}_{\ell n}(u)\langle \hat{p}_n(u)\rangle\} \tag{36}$$

The effect of averaging over all possible configurations is to make the system translationally invariant, so that these equations can be solved by transforming to k space (just as we did for nondisordered crystals), and we find (taking $\langle p_n(0)\rangle = \delta_{no}$)

$$\langle p_n(u)\rangle = \frac{1}{N}\sum_k \frac{e^{i\underset{\sim}{k}\cdot\underset{\sim}{R}_n}}{u + [\hat{M}(0,u) - \hat{M}(k,u)]} \tag{37}$$

where

$$M(k,u) = \sum_n e^{ik\cdot(\underset{\sim}{R}_n-\underset{\sim}{R}_\ell)} M_{n\ell}(u) \qquad (38)$$

We can define a generalized diffusion kernel D(k,u) by

$$\hat{D}(k,u) \equiv \hat{M}(0,u) - \hat{M}(k,u) \qquad (39)$$

and we find that the long time diffusion constant is given by

$$D = \frac{1}{2d}\left[\frac{d^2}{dk^2}\, D(k,u)\right]_{k=0,\ u=0} \qquad (40)$$

Thus the averaging procedure has produced an effective medium in which the excitation moves. In this medium, there is a memory term in the dynamical equation.

We can rearrange the GME into another equation, also often used to model disordered systems: the continuous time random walk equation [13] or CTRW. In this model, a probability density distribution for jumping from $\underset{\sim}{R}_n$ to $\underset{\sim}{R}_m$ at time t is given by $\Psi(\underset{\sim}{R}_n-\underset{\sim}{R}_m,t)$ and the probability for finding the excitation at $\underset{\sim}{R}_n$, given that it was at the origin initially is

$$\langle p_n(\underset{\sim}{R}_n,t)\rangle = \Phi(t)\delta_{n,o} + \sum_{m\neq n}\int_o^t d\tau\ \psi(\underset{\sim}{R}_m-\underset{\sim}{R}_n,\ t-\tau)\langle P(\underset{\sim}{R}_m,\tau)\rangle \qquad (41)$$

where $\Phi(t)$ is the probability that the excitation has not left the initial site at time t. By Laplace and Fourier transforming this equation and comparing it to Eq. (37), we find that (in Laplace variable u)

$$\tilde{\psi}(R_m,u) = N^{-1}\sum_k \tilde{S}(k,u)\, e^{ik\cdot \underset{\sim}{R}_m} \qquad (42)$$

where

$$\tilde{S}(k,u) = \frac{\tilde{M}(\underset{\sim}{k},u)}{u + \tilde{M}(\underset{\sim}{0},u)} \qquad (43)$$

The probabilities are given by

$$\langle p_n(u)\rangle = \frac{1-S(\underset{\sim}{0},u)}{Nu}\sum_k \frac{e^{ik\cdot \underset{\sim}{R}_n}}{1-S(k,u)} \qquad (44)$$

and so in the CTRW, the Laplace transform of the mean square displacement is given by

$$\langle R^2(u)\rangle = \frac{1}{u(1-S(\underset{\sim}{0},u))}\sum_n R_n^{\,2}\ \tilde{\psi}\ (R_n,u) \qquad (45)$$

and the (time dependent) diffusion coefficient is given as

$$D(u) = \frac{(1/2d)}{1-S(\underset{\sim}{0},u)}\sum_n R_n^{\,2}\ \tilde{\psi}\ (\underset{\sim}{R}_n,u) \qquad (46)$$

Thus in the CTRW approach, we must find $\tilde{\psi}(\underset{\sim}{R}_n,u)$ in order to obtain expressions for the diffusion coefficient and site probabilities. In the GME approach, we must find expressions for the kernels $\tilde{M}(\underset{\sim}{k},u)$. But, it should be emphasized that the information in one formal theory can be found from that in the other. Unfortunately, it is impossible in all but the simplest (and least interesting) models to find exact expressions for these quantities. We are then forced to approximate in order to go further. It turns out that for certain models one form of the theory is easier to use than the other form. We will illustrate this in the following examples.

### III.B. Effective Medium Approximation [21,24,25]

As we said above, averaging over all configurations has produced an effective medium with memory. One direct approach to approximate this exact effective medium is to limit the range of the kernels $\tilde{M}_{n\ell}(u)$, see Eq. (36), to a small distance and solve for these in a self-consistent fashion. For example, suppose the original system is a partially filled lattice in which only nearest neighbor transfer rates are allowed in Eq. (26) (and for simplicity, we take a d-dimensional lattice with equal transfer rates to all z of the nearest neighbors):

$$W_{mn} = \begin{cases} W_o & m,n \text{ nearest neighbors} \\ 0 & \text{otherwise} \end{cases} \tag{47}$$

The transport in this system will exhibit a percolation transition: below some value $p_c$ of fraction of sites occupied on the lattice, there will be a bound on the mean square displacement, so that the long time diffusion constant is zero. We can approximate this dynamics in the GME formalism by replacing the $\tilde{M}_{n\ell}(u)$ in the GME by a <u>nearest neighbor</u> effective rate, $\tilde{W}_E(u)$, so that

$$\tilde{M}_E(k,u) = \tilde{W}_E(u) \sum_{nn} e^{ik\cdot \underset{\sim}{R}_{nn}} \tag{48a}$$

$$\tilde{M}_E(\underset{\sim}{0},u) = z\tilde{W}_E(u) \tag{48b}$$

where the sum is over the nearest neighbors of any site. In order to determine $\tilde{W}_E(u)$, we must find a self-consistent equation for it. There are of course many possibilities for this. Following earlier workers [21,24,], we choose a method closely related to the coherent potential approximation (CPA) used to approximate the density of electronic states in disordered systems [37]. We take the effective medium (represented by Eq. (48)) as the zeroth order description and represent the exact equations (Eq. (29)) as a sum of this and "fluctuations" from this zeroth order description. It is easier to work in Laplace transforms for which the exact p(u) are given by (we have gone back to a vector description for succinctness)

$$\underset{\sim}{p}(u) = (u\,\underline{\underline{1}} + \underline{\underline{V}})^{-1}\ p(0) \equiv \underline{\underline{G}}(u)p(0) \tag{49a}$$

The matrix $\underline{\underline{G}}(u)$ is now written as

$$\underline{\underline{G}}(u) = [u\,\underline{\underline{1}} + \underline{\underline{M_E}}(u) + \delta\underline{\underline{V}}]^{-1} \tag{49b}$$

with $\delta\underline{\underline{V}} = \underline{\underline{V}} - \underline{\underline{M_E}}(u)$. We can expand $\underline{\underline{G}}(u)$ in terms of $\underline{\underline{G_M}}(u) = [u\,\underline{\underline{1}} + \underline{\underline{M_E}}(u)]^{-1}$ as

$$\underline{\underline{G}}(u) = \underline{\underline{G_M}} + \underline{\underline{G_M}}\ \underline{\underline{T}}\ G_M \tag{50}$$

where the T matrix is expressed in terms of bond t-matrices, $t_{nm}$ [24]:

$$t_{nm} = \frac{W_E-W_{nm}}{1-2(W_E-W_{nm})((G_M)_{nn}-(G_M)_{nm})} \tag{51}$$

Since the effective medium is translationally invariant, we can easily find $(G_M)_{nm}$, etc. The self-consistency condition is to average Eq. (51) over the distribution of $W_{nm}$'s and set the average to zero. In this way, the "scattering" of the excitation due to fluctuations in the nearest neighbor transfer rates is minimized in the same way as the scattering of the wave function is in the CPA. Using the effective medium $G_M$, we find

$$\langle t_{nm}\rangle = \int \rho(W) \frac{(W_E-W)dW}{1-2(W_E-W)(1-uG_o)/zW_E} = 0 \tag{52}$$

Here $\rho(W)$ is the distribution function of nearest neighbor transfer rates $W_{nm}$ (due to the occupation probabilities), $G_o = (G_M)_{nn}$ and z is the number of nearest neighbors in the lattice.

If we take a model in which the probability that the bond between n and m is present (i.e. $W = W_o$) is p and the probability that that bond is absent (i.e. $W = 0$) is $(1 - p)$, then we find from Eq. (52)

$$W_E(u) = W_o \frac{p - \frac{2}{z}(1-uG_o(u))}{1 - \frac{2}{z}(1-uG_o(u))} \tag{53}$$

This predicts a (long time) diffusion constant, D, which vanishes for $p < 2/z$ and is linear in $p - 2/z$ for $p > 2/z$. Thus the EMA predicts bond percolation with a critical concentration of bonds equal to $2/z$, independent of dimension. This result was found earlier in the percolation problem by Kirkpatrick [38]. This result is not exact for the bond problem, but is a reasonable approximation in almost all cases [21]. In addition to the diffusion constant, the approximate time dependence of $\langle R^2(t)\rangle$ and $D(t)$ can be found using the EMA [21]. The dependence of D and $R^2$ on time and $p - 2/z$ as p approaches $2/z$ (the percolating cluster) can also be found approximately by this method. Although the results are not exact, the capability of the EMA to get useful approximations in a simple way is excellent.

If instead of a percolation model, we take a specific form for $\rho(W)$ in Eq. (52), and if $uG_o(u)\to 0$ as $u\to 0$, then we can find the diffusion constant, D, from Eq. (52). In particular, in a one-dimensional system, we find $D \propto \langle W^{-1}\rangle^{-1}$ where the average is over the distribution $\rho(W)$.

### III.C. CTRW Approximations

We return to the discussion of the CTRW equations and note that if we had an approximate form for the waiting time distribution functions $\psi(Rn,u)$, we could find a form for D from Eq. (46). A number of years ago, Scher and Lax [13] suggested a route to $\psi(R_n,t)$. They noted that the probability of remaining at the initial site, $\Phi(t)$ (see Eq. (41)) must be the form we have already discussed for the donor-acceptor problem. But in addition, by comparing eq. (41), (42), and (44), we can make the identification that

$$\dot{\Phi}(t) = - S(0,t) = -\sum_m \psi(R_m,t) \tag{54}$$

Since, from Eq. (4)

$$\Phi(t) = \prod_i [(1-p) + p\, e^{-W_{i\alpha} t}] \tag{55}$$

we can identify

$$\psi(R_m,t) = pW(R_m)e^{-tW(R_m)}\{\prod_{n\neq m} [(1-p) + p\, e^{-W(R_n)t}]\} \tag{56}$$

or in the limit of small concentrations

$$\psi(R,t) = pW(R)\, e^{-tW(R)}\Phi(t) \tag{57}$$

and $\Phi(t)$ given by Eq. (7). We may now evaluate the mean square displacement using Eq. (45) and the diffusion coefficient using eq. (46). As an example, choose the multipolar transition rate given by $W(r) = \alpha/r^s$ the we saw above that (Eq. (9))

$$\Phi(t) = \exp - Bt^{d/s} \tag{58}$$

The Laplace transform of the diffusion coefficient $\tilde{D}(u)$ is then given by Eq. (46) (and Eqs. (54) and (57)) as

$$\tilde{D}(u) = \frac{1/2d}{u\tilde{\Phi}(u)}\; L\{c \int d^dR R^2 W(R)\, e^{-tW(R)}\Phi(t)\}\quad . \tag{59}$$

Using the multipolar form for W(R),

$$\int d^dR R^2 W(R) e^{-tW(R)} \sim t^{(d+2/s)-1}\, e^{-Bt^{d/s}} \tag{60}$$

We can immediately find the short and long time dependences of D from these equations. At short times

$$D(t) \sim t^{(d+2)/s-1}\quad , \tag{61}$$

and at long times D is a constant but depends on concentration of occupied sites as $c^{(s-2)/d}$.

These results agree with a density expansion by Haan and Zwanzig [11] of the Förster energy transfer problem: $W(R) = 1/\tau(R_o/R)^6$. By a clever scaling argument these authors showed that the mean square displacement of an excitation starting at the origin and moving through a randomly arranged array of donor molecules is given by

$$\langle R^2(t)\rangle = t^{1/3}\; F(ct^{1/2}) \tag{62}$$

where F is a function of the variable $ct^{1/2}$ the first few terms of which are known. Thus at short times, $\langle R^2(t)\rangle$ varies as $ct^{5/6}$ and at long times, if $\langle R^2(t)\rangle$ varies as t then D varies with concentration as $c^{4/3}$. Their arguments are easily generalized to $W(R) = 1/\tau(R_o/R)^s$ in d-dimensional space leading to the results found using the CTRW. This shows explicitly that the dependence of the dynamics on concentration and time are inevitably linked.

A number of authors have applied the CTRW technique to problems of diffusion in random media, othere have used density expansions of the kernels appearing in the GME, and while these calculations agree with one another qualitatively, the correct value of D is still uncertain in any model with long range transfer. Burshtein [16] has recently reviewed the various theoretical models for energy transfer in disordered systems.

### III.D. Anomalous Diffusion and Trapping

A standard approximation in the CTRW is to make the assumption that (see Eq. (42))

$$\psi(R_m,t) = \underline{P}(R_m)\psi(t) \tag{63}$$

Then

$$\tilde{S}(k,u) = \lambda(k)\,\tilde{\psi}(u) \tag{64}$$

where

$$\lambda(k) = \sum_m e^{ik\cdot R_m}\,\underline{P}(R_m) \quad . \tag{65}$$

Then (see Eq. (45))

$$\langle R^2(u)\rangle = \frac{1}{u[1-\tilde{\psi}(u)]}\;\tilde{\psi}(u)(\sum_n R_n^2\underline{P}_n) \tag{66}$$

since $\Sigma\underline{P}(R_m) = 1$ (The total probability of making any jump must be 1.) and

$$D(u) = \frac{(\Sigma R_n^2\underline{P}_u)}{2d}\;\frac{\tilde{\psi}(u)}{1-\tilde{\psi}(u)} \tag{67}$$

Now the time dependence of D(u) is governed solely by $\tilde{\psi}(u)$. In particular, the long time dependence of D(t) is determined the small u dependence of $\tilde{\psi}(u)$. $\psi(t)$ represents the probability distribution of waiting times; if this distribution has a long time tail, there may be anomalous diffusion. Consider first the non-anomalous case, then

$$\tilde{\psi}(u) = \int_0^\infty dt\; e^{-ut}\psi(t) = 1 - u\int_0^\infty dt\; t\,\psi(t) + \cdots \tag{68a}$$

$$= 1 - u\,\tau_1 + \cdots \tag{68b}$$

If $\tau_1$ is finite, then

$$D(u) = \frac{(\Sigma R_n^2\underline{P}_n)/2d}{u\tau_1} \qquad u\to o \tag{69}$$

so that for long times

$$D = (\Sigma R_n^2\underline{P}_n)/2d\tau_1 \quad . \tag{70}$$

If, however, the first moment of $\psi(t)$ is infinite, say for example

$$\psi(t) \sim t^{-1-\beta}\ ,\ t\to\infty \qquad 0 < \beta < 1 \tag{71}$$

then

$$\psi(u) = 1 - \Gamma(1-\beta)u^{\beta}/\beta + \cdots \tag{72}$$

and

$$D(t) \sim t^{\beta-1} \tag{73}$$

Thus $\langle R^2(t)\rangle \sim t^{\beta}$ and the diffusion is anomalous. By the way, this approximation for $\psi(t)$ yields

$$\Phi(t) \sim t^{-\beta} \tag{74}$$

for the decay law of an excitation due to donor-acceptor transfer.

Montroll and Scher chose the form of Eq. (71) for $\psi(t)$ in their study of dispersive transport in amorphous materials. It is the extremely long waiting times (or trapping times) which cause the dispersion in the transport. In our discussion, this yields a time dependent diffusion coefficient (Eq. (73)) which decays to zero at long time. The form for $\langle R^2(t)\rangle$ (i.e. proportional to $t^{\beta}$, $\beta < 1$) is unusual; it is interesting to ask in what circumstances such a form can come about.

Another problem of current interest is the trapping of an excitation as it hops through a disordered system. We think about the excitation as a random walker which is removed from the problem if it walks onto a trap site. The trap sites are randomly arranged on a lattice with probability c of being on any particular site. This problem has been extensively treated in the literature [27,28] in terms of $R_n$, the number of distinct sites visited by the walker after n steps. The survival probability, $\Phi_n$, is then the average over all realizations of the walk of the survival probability for each realization:

$$\Phi_n = \langle (1-c)^{R_n-1} \rangle = \langle e^{(R_n-1)\ln(1-c)} \rangle \tag{75}$$

$R_n$ is a stochastic variable, and the average in Eq. (75) cannot be done in general. The standard approximation for small c (low concentration of traps) is to write

$$X_n = e^{-cS_n} \tag{76a}$$

where $S_n = \langle R_n \rangle$, the mean number of distinct sites visited after n steps. This is a known function of dimensionality and lattice.

The above was derived for random walks with a constant jump time. If we allow for a jump-time distribution as in the CTRW, then the survival probability is

$$X(t) = e^{-cS(t)} \tag{76b}$$

and we can define the decay rate of the excitation to be

$$k(t) = -\frac{\dot{X}(t)}{X(t)} = c\dot{S}(t) \tag{76c}$$

Here S(t) is related to the $\tilde{\psi}(u)$ we introduced above (Eq. (64)) by

$$\tilde{S}(u) = \sum_{n=0} S_n[\tilde{\psi}(u)]^n \frac{(1-\tilde{\psi}(u))}{u} \tag{77}$$

Other approximations to Eq. (75) are possible. In particular, at not too long times we can go to the second cumulant to find [32]

$$X(t) \cong e^{-cS(t) + c^2\sigma^2(t)/2} \tag{78a}$$

The properties of $S_n$ are known for d-dimensional lattices [27,28] and thus we can find the long time behavior of X(t) for a variety of situations.

Blumen and Zumofen [43] have carried out extensive simulations of trapping rates and survival probabilities, and compared them with the approximate results mentioned above as well as other approximations. For example, these authors found that if $\psi(t)$ has a finite first moment (Eq. (68)) then, in 3 dimensions, X(t) was exponential in time (for not too long times). If however $\psi(t)$ has a long time algebraic tail (Eq. (17)), then $\tau_1$ does not exist and the survival probability $X(t) \sim t^{-\beta}$.

The asymptotic decay of X(t) for very long times has been discussed by a number of authors [40-42] and using rather general arguments, it is found that

$$X(t) \sim \exp - t^{(d/d+2)} \tag{78b}$$

This long time decay is dominated by the probability of the excitation being born in a large trap-free region. It turns out that although this is correct, it occurs for such long times that it is unlikely to be observable in practice. In fact, except for 1 dimension it is difficult to see even in simulations.

Other problems, related to trapping, have been studied in the past few years. These are the bimolecular reactions $A + A \to 0$ and $A + B \to 0$ with rate constant k. The kinetics of these under the assumption of a "well-stirred" reactor are easy to find so that in the first

$$A(t) = A_o(1+2A_okt)^{-1} \sim 1/t \tag{79a}$$

and in the second, for $A_o = B_o$,

$$A(t) = A_o(1+A_okt) \sim 1/t \tag{79b}$$

If the well-stirred condition is not correct, then there are strong dependences on disorder for the long time limit of these processes. For example, for A's walking on regular lattices, it is found (by simulation) that for the first case

$$A(t) \sim [cS(t)]^{-1} \tag{80}$$

describes the dynamics very well. However, for the second case, another problem arises. Spatial fluctuations in the concentrations of A and B are enhanced by the chemical reaction, and regions containing only A or only B molecules appear. In this case, it turns out that the behavior (for regular lattices) of A(t) starts out as Eq. (80) but crosses over to a slower decay at longer times.

## IV. OPTICAL LINE SHAPES IN DISORDERED SOLIDS

In this section, we will deal with two topics: A) the optical line shape of molecules in a solid in the presence of weak disorder at low T and B) the homogeneous line shape of a guest molecule in a glass at low T.

Both of these have their genesis in trying to answer specific experimental questions, so we will present them in that manner.

### IV.A. Optical Line Shape: Weak Disorder [44,45]

The optical absorption spectroscopy of molecular crystals at very low temperature has been of interest for many years [46], but until recently, the true shape of the optical lines at very low temperature have been obscured by various effects. Recently, Port [45] was able to determine the absorption line of a particular molecular crystal at temperature below 2 K with such clarity that, I believe, we are seeing the scattering of the excitation by isotopic impurities in the solid. This is a case in which we know so many of the parameters that a clear comparison between experiment and theory is possible.

The molecule is 1,4-dibromonaphthalene (or DBN). It crystallizes, as do many planar molecules, in a form which exhibits linear stacks of molecules. The optical spectroscopists have discovered that, in the pure material, the lowest energy electronic excitation moves down these one-dimensional stacks preferentially (the transfer matrix element for off the stack is $\sim 10^{-4}$ of that for down the stack), so that the excitons are very nearly one-dimensional. At very low T, the spectroscopists have found that the optical absorption spectrum is a highly asymmetric line (independent of T for the lowest temperatures). They guessed that the cause of the asymmetry was impurities of DBN containing $C^{13}$. Since the natural abundance of $C^{13}$ is 1%, approximately 10% of DBN molecules will have one $C^{13}$ in it. Because of zero point vibrational energy effects, the optical absorption of these molecules are slightly blue shifted from that of the "pure" DBN. This energy difference causes scattering of the exciton and changes the optical spectrum. Another way to think about it is to say that these impurities break down the translational symmetry and cause intensity redistribution in the spectrum.

We describe the Hamiltonian of the system as

$$H = \sum_n \epsilon_n |n\rangle\langle n| + \sum_{n,m} J_{nm} |n\rangle\langle m| \tag{81}$$

where $\epsilon_n$ is the excitation energy at site n, $|n\rangle$ is the localized state with excitation on site n and $J_{nm}$ is the excitation transfer matrix element. We assume (because the spectroscopists tell us) that $J_{nm}=0$ unless n and m are nearest neighbors. If all the $\epsilon_n$ are equal, the eigenstates of H can be written down immediately (assuming periodic boundary conditions) as

$$|k\rangle = \frac{1}{\sqrt{N}} \sum_n e^{ikn} |n\rangle \tag{82}$$

We have written this in one-dimensional notation for convenience. The eigenvalue corresponding to $|k\rangle$ is $2J\cos k$ in one dimension. For the impure crystal, we assume that J is unchanged and independent of isotopic species. The optical line shape as a function of energy, I(E) is given by an average over all possible configurations of impurities of the imaginary part of the k = 0 Green function:

$$I(E) = \mathrm{Im}\langle G(k=0,E)\rangle_c \tag{83}$$

and

$$G(k,E)\ \langle k|(E-H-i\delta)^{-1}|k\rangle \tag{84}$$

with $\delta$ a small positive number. For the pure system, this gives a delta function line shape centered at $E = \varepsilon+2J$ (or if $\delta$ is the inverse of the radiative lifetime, a sharp Lorentzian of width $\delta$). In the specific case of DBN, the lifetime is quite long, so that $\tau^{-1}$ is quite small. The effect of the impurities is to spread intensity from the zeroth order k=0 level to the other energies in the band, by the mixing of this state into other states. One way of carrying this out is to write

$$\langle (E-H-i\delta)^{-1}\rangle_c = [E-H_{eff}(E)]^{-1} \quad , \qquad (85)$$

where $H_{eff}(E)$ is some complex function of E. A formally exact expression for $H_{eff}(E)$ can be written, but since it cannot be evaluated exactly, we will not bother. Instead, we will find an approximate form for $H_{eff}(E)$ using the coherent potential approximation [37]. We write ($\bar{\varepsilon}$ is the configurational average of the excitation energy)

$$H_{eff} = [\bar{\varepsilon}+\sigma(E)] \sum_{n} |n\rangle\langle n| + \sum_{n,m} J_{nm}|n\rangle\langle m| \qquad (86)$$

and $H = H_{eff} + V$ with

$$V = \sum_{n} [\varepsilon_n-\bar{\varepsilon}-\sigma(E)]|n\rangle\langle n| \equiv \sum v_n|n\rangle\langle n| \qquad (87)$$

The exact Green function can now be expanded in terms of the zeroth order (effective) Green function and the t matrices, and the site diagonal t is

$$t_{nn} = v_n[1-v_nG^{(0)}_{nn}]^{-1} \qquad (88)$$

where

$$G^{(0)}_{nn} = \langle n|(E-H_{eff})^{-1}|n\rangle \qquad (89)$$

We now set the average of t equal to zero:

$$\sum_{\alpha=1}^{p} c_\alpha t^{(\alpha)} = 0 \qquad (90)$$

where $c_\alpha$ is the concentration of each isotopic species. This gives, after some manipulation

$$\sum_{\alpha=1}^{p} \frac{c_\alpha}{1-v(\alpha)G^{(0)}_{nn}(E)} = 1 \qquad (91)$$

This is the CPA equation. Note that since both $v^{(\alpha)}$ and $G^{(0)}_{nn}$ contain $\sigma(E)$, this must be solved self-consistently. We have solved this for the parameters of DBN (all the relevant parameters are given in ref. [45]). For this system, the energy defects (i.e. $\varepsilon^{(\alpha)}-\varepsilon_{pure}$) are small compared to J, being at most 0.2 J, thus we expect the CPA to be a reasonable description. We have computed the line shape in this way and compared it to the experiment. There is almost perfect agreement in shape and overall width between the two. This suggests that, at least in certain cases, it is possible to find a zero temperature line shape dominated by weak disorder effects such as isotopic scattering rather than other defect scattering. Ⓐ

## IV.B. Homogeneous Line Widths of Molecular Transitions in Glasses [47]

When a small concentration of guest molecules is placed in a host, the optical absorption spectrum of these is inhomogeneously broadened because each molecule is in a different environment. If the host is crystalline, it is possible to observe the homogeneous line shape of the molecular absorption using a variety of techniques such as flourescence line narrowing, photon echos, and hole burning. When the homogeneous linewidth is measured as a function of temperature, the mechanism of homogeneous broadening or dephasing can be elucidated in the more favorable cases. For example, local mode or librational mode dephasing varying as $e^{-\omega_o/kT}$ at low temperature has been observed, as well as acoustic phonon dephasing by Raman processes (varying as $T^7$) have been identified.

When the host is a glass, things are not so easy. First of all, the inhomogeneous broadening is quite large, often complicating the interpretation of the more complex experiments. Secondly, when the homogeneous linewidth is uncovered, unusual and totally unexpected temperature dependences have been found. This field is of sufficient current interest that an issue of Journal of Luminescence was recently devoted to the problem of hole burning in optical lines in glasses.

The hole burning experiment is the following: an inhomogeneously broadened line is irradiated at a particular frequency by a narrow band laser for some time, and then the optical absorption recorded with low intensity light. A hole is found in the inhomogeneous line at the frequency of the laser. When care is taken not to heat the sample, etc., the hole shape is assumed to be related to the homogeneous line shape of the molecules at the laser frequency by a simple convolution. We assume that the experiments have been done well, and look at the homogeneous linewidths $\gamma(T)$. We find that they vary with temperature as

$$\gamma(T) = \gamma_o + aT^{1+\gamma} \quad \alpha \tag{92}$$

where $\gamma_o$ is the inverse lifetime of the transition and $\alpha$ is a parameter which depends (slightly) on system but $0 < \alpha < 1$. For many systems (that is many chromophores in different glasses) $\alpha = 0.3$.

This unusual temperature dependence has been ascribed to the presence in glasses of low frequency excitations, called two level systems (TLS), which have been invoked to explain the low temperature heat capacity and thermal conductivity of glasses. It was discovered about 15 years ago that at very low $T(T<1K)$, glasses have heat capacities varying approximately linearly with T. An explanation was presented by Phillips [48] and by Anderson et al. [49] based on the presence of many barriers and disorder in glasses, which would give rise to many tunneling states. If the levels on either side of the barrier differed in energy by $\Delta$ and there was a tunneling matrix element $K/2$ between them, then the energy separation between the final two levels would be $(\Delta^2+K^2)^{1/2}$. If we treat these as a TLS, then the intense energy of the glass at temperature T $(=1/k\beta)$ would be

$$E(T) = \int_o^{\omega_c} d\omega\rho(\omega)\omega \; \frac{e^{-\beta\omega}}{1+e^{-\beta\omega}} \tag{93}$$

where $\rho(\omega)$ is the density of states of the TLS and $\omega_c$ is some cutoff energy. If we assume that $\rho(\omega)$ varies as $\omega^\alpha$ at low $\omega$, then at temperatures low compared to $\omega_c/k$, $E(T) \sim T^{2+\alpha}$ and $C_v \sim T^{1+\alpha}$. the standard model is $\alpha = 0$, but no one really knows for certain.

Although the exact nature of the TLS is still not known, this conjecture has proven to be of great utility in explaining phonon scattering, thermal conductivity etc. in glasses at low T. When the hole burning experiments were done, it was naturally assumed that the TLS were implicated, even though these experiments were usually done at temperatures above 1K (and the specific heat experiments were done below 1K). The basic model is straightforward: consider an optical transition between two levels and assume that there is a TLS strongly interacting with that optical system. This yields a 4-level system. Assume further that the TLS is slightly changed (in energy and eigenstates) when the chromophore is excited from what it is when the chromophore is in the ground state. Now, if phonons can "flip" the TLS during an optical transition of the chromophore, the optical transition will experience some frequency modulation, or dephasing. This is the origin of the TLS induced homogeneous width for the optical trasition. The TLS is changed when the chromophore is excited because the TLS will have a dipole moment and when this interacts with the chromophore, the energy depends on the state of the chromophore.

This model can be treated using the theory of spectral diffusion [50] or the standard weak coupling (Redfield) theory [47] for a single TLS. The result must then be averaged over a distribution of TLS parameters. When this is done, it is found that the homogeneous linewidth depends on the temperature at low T as $T^{1+\alpha}$, where $\alpha$ is the exponent in the density of states of the TLS. This suggested to many workers that there was a (more or less) universal exponent for the TLS distribution of $\alpha \approx 0.3$. In fact, experimentally it was found that the specific heat of glassy silica below 700 mK varies as $T^{1.2}$, as well. Recently, a number of authors [51] have suggested that more careful averaging even over the standard parameters of the Anderson-Phillips model will give the $T^{1.3}$ dependence at very lot T.

In addition, other authors [47] have suggested that the hole widths and the photon echo decays are really sums of two mechanisms - one for the TLS (and nearly linear in T) and one for a direct phonon mechanism (such as Raman scattering or local mode scattering).

Finally, there is a recent speculation that the true cause of the anomalous exponent is due to the fractal nature of the glass [52].

## V. FRACTALS AS MODELS OF DISORDERED SYSTEMS [53-63]

In the last five years, there has been an explosion of interest in fractals, as can best be seen by the number of conferences and papers devoted to the subject. This recent interest has its genesis in the work of Mandelbrot [53], and can in part be understood by the simplicity and beauty of both the science and the figures which are produced to illustrate the concepts. Very recently, a number of articles [64] have suggested that it was time to take stock of what had been done and to make certain that physics was the principal concern.

In this section, I will selectively review the work of others on the use of fractals to model disordered systems. In particular, I will be concerned only with the use of these structures for the modelling of the effect of disorder on dynamical processes in disordered systems.

### V.A. Description of Fractal Structure

In 1919, Hausdorff suggested a way to generalize dimension by use of what we now call scaling. Suppose a very complex curve, for example the

Sicilian coastline, were to be measured by sticks of different length, $\ell$. To do the measurement, we lay the stick down end-to-end along the coast. By this method, irregularities of length less than $\ell$ are smoothed out. The number of sticks of length $\ell$ needed to cover the coast line is $N(\ell)$. For a straight line, $N(\ell)$ depends on $\ell$ in a simple linear way: if we change the size of the stick from $\ell$ to $\ell/a$ we find

$$N(\ell/a) = (\frac{\ell}{a})N(\ell) \tag{94}$$

We can measure area in this manner as well using squares of side length $\ell$ or a to find that the number of squares needed in the first case is $(\ell/a)^2$ times the number needed in the first. In general, if we are measuring in units of $\ell^d$ we find that the number of units needed scales as $(\ell/a)^d$. In our usual world view, d can be an integer. However, Hausdorff and more recently Mandelbrot have shown us how to generalize this. A simple example is the Koch snowflake, which is formed by start- with an equilateral triangle and adding, in the middle of each side, an equilateral triangle of 1/3 the side length of the original. This produces a star of David. The process is repeated at 1/3 the scale to all the sides of the star. And so on, indefinitely. Our measurement process is blind to detail smaller than the stick. Then every time we measure the perimeter of this snowflake with a stick 1/3 the length of the previous stick, we find the number of sticks needed is 4 times the previous number. That is

$$N(\ell/a) = (\ell/a)^{\overline{d}}N(\ell) \tag{95}$$

where $\overline{d} = \log[N(\ell/a)/N(\ell)]/\log(\ell/a) = \log 4/\log 3 = 1.26$ in our case! Mandelbrot introduced the word fractal for objects with noninteger dimension.

Another example is the Sierpinski gasket which can also be formed from equilateral triangles, but with a different method. Stack three equivalent triangles together to form a new equilateral triangle with a hole in its center. Now stack three of these to form a new triangle with a larger hole in the center. Continue until exhausted. If we measure the area of such an object, we note that every time we decrease our length scale by 2 we "see" an area which increases by 3 (not 4 as in normal structures) so that $\overline{d} = \log 3/\log 2 = 1.58$. The Sierpinski gasket is a favorite toy for modelling disorder because we may assume a site exists on every vertex and bonds between every pair of near neighbors.

Regular fractals of this type come in many varieties. The dimension $\overline{d}$ is called the fractal or Hausdorff dimension (the space in which the structure is embedded has an integer dimension, so this particular Sierpinski gasket has fractal dimension 1.58 and embedding dimension 2).

Based on the construction we have outlined, fractals have the property of self-similarity. That is they look the same on every length scale. Every time we increase the magnification, the structure looks the same. (This is just the condition necessary to introduce the fractal dimension.) Real disordered systems are clearly not self-similar on all length scales; however, it may be a good approximation to assume it to be so over a restricted set of scales.

We do not restrict the term fractal only to geometric properties. This allows us to introduce fractal dimensions for many properties of random systems. For example, random walks can be considered to be fractal in certain properties.

Consider a random walker in a d dimensional regular lattice. Assume that at each step of the walk a molecule is placed on the site visited, and forget about self-avoidance. Then after N steps (or time $t = N\tau_1$) we find N molecules on the path of walker. This path on the average has a length, L, proportional to $N^{1/2}$. Therefore the mass of the path M is proportional to $L^2$, i.e. it is a fractal of dimension 2.

If we do not allow intersections, i.e. we have a self-avoiding walk, then L is proportional to $N^\nu$, $\nu = 0.6$ on 3-dimensional lattices and $\nu = 0.75$ on 2-dimensional lattices, so that the mass of the path $M \sim L^{1/\nu}$, i.e. a fractal dimension of 1.67 in 3d and 1.33 in 2d.

Another statistical fractal is the percolation cluster. At the percolation threshold, $p = p_c$, the network of occupied sites is self-similar, that is, it looks the same on all length scales large compared to the bond length and short compared to the correlation length $\xi$. Since $\xi$ varies as $(p-p_c)^{-\nu}$ as p approaches $p_c$, the object is self-similar on all scales at the percolation edge. By scaling arguments, it is found that the number of sites on the percolation network within a radius R of a randomly chosen origin is given by $N(R) \propto R^{\bar{d}}$ where $\bar{d} = d-\beta/\nu$. The exponent $\beta$ is defined by the probability of a site belonging to the infinite cluster, $P_\infty - (p-p_c)^\beta$.

A final example of a statistical fractal are structures grown by diffusion limited aggregation, which have been studied in great detail in recent years [54].

How do experimenters tell if a real system can be described as a fractal? In practice, one measures a quantity, say the density, of objects of various radius and plots the log vs. the log of the radius, hoping for a straight line.

For example, if a real object has a mass depending on radius as $R^{\bar{d}}$, then the density depends on $R^{\bar{d}-d}$; that is, the bigger it gets the more tenuous it becomes. Scattering measurements are often the method of choice to determine the quantities we are after. Clearly, if the density scales in an unusual manner with R, the scattering as a function of $\underset{\sim}{K}$ will also scale with $\underset{\sim}{K}$ in a complementary manner [55]. Since we do not restrict attention to mass or volume, one fractal dimension is insufficient to determine all the quantities which we measure, Stanley [56] has discussed in his Cargese talk, 10 fractal dimensions. Happily, not all are independent quantities.

In the study of dynamics on fractals, for example, there has been considerable discussion in the past 10 years about a random walker walking on a fractal [57], for example the percolation cluster. Since the walker goes into dead-ends a lot of the time and must retrace its steps, we expect anomalous diffusion, i.e. $\langle R^2(t)\rangle \sim t^{2\gamma}$, with $\gamma = \frac{1}{d_w} < \frac{1}{2}$. Here we have introduced the dimension $d_w$ often written as $2 + \theta$. The number of distinct sites visited on the walk scales with the Hausdorff or fractal dimension, $\bar{d}$; thus the number of distinct sites scales as $t^{\bar{d}/dw} = t^{d_s/2}$. Alexander and Orbach [58] suggested that the dimension $d_s$ be called the spectral (or fracton) dimension. By a scaling argument they conjectured that the density of modes on the fractal would scale as $\omega^{d_s-1}$ (instead of $\omega^{d-1}$ in d dimensional Euclidean space). Using known values of various exponents, they found $d_s \cong 4/3$ for percolation clusters embedded in d dimensional lattices. This led to a number of studies which have suggested that $d_s$ is not simply given by 4/3 for all d, but is close to that value and attains it for $d>6$. Later studies also refined their argument (because it was based on an isotropic model inappropriate for elastic modes) and redefined the spectral dimension [55]. In any case, the basic idea that the mode density of states varies on a fractal as $\omega^{d_s-1}$, i.e. that the modes, which are localized, have an unusual form suggested that relaxation processes in such systems should exhibit interesting time or temperature dependences. For example, Stapleton et al. [59] suggested that the unusual temperature dependence of the spin lattice relaxation found in proteins was caused by the fractal structure of the protein. These authors used the Hausdorff dimension to fit their data; Orbach suggested using the spectral dimension instead. Unfortunately, the agreement between this theory and experiment is not very good. Recently, Elber and Karplus [60] suggested a model for calculating the spectral density in a protein directly and saw little evidence fo fractal or fracton behavior in their results.

### V.B. Transport on Fractals [61]

We will now discuss how fractal geometry changes the dynamics of the various processes we discussed earlier.

First, we discuss donor-acceptor transfer to acceptors arranged on a fractal. Recall Eq. (8) for the probability, $\Phi(t)$, of the excitation remaining on the donor. If the acceptors are arranged on a fractal with Hausdorff dimension $\bar{d}$, the density of sites varies as $r^{\bar{d}-1}dr$, so the result is immediate for multiple transfer, $w(r) \sim r^{-s}$:

$$\Phi(t) = \exp\{-B_s \cdot c t^{\bar{d}/s}\} \tag{96}$$

and

$$\Phi(t) = \exp\{-B_\gamma \, \ell n^{\bar{d}} \, (W_0 t)\} \tag{97}$$

This has been tested by the simulations of Blumen and Zumofen. The agreement with (96) and (97) is very good. A few years ago, Even et al. [62] put the donors and acceptors in a porous glass and measured the decay time of the donors (the donor was rhodamine 6G, the acceptor malachite green). When this was compared to the same system in a solid solution, these authors suggested that the structure in which the molecules sat was a fractal of dimension $\bar{d} = 1.74$.

In recent years, Klafter, Blumen and Zumofen [63] simulated a series of random walks on Sierpinski gaskets embedded in Euclidean dimension of d = 2-6. These all have spectral dimensions $d_s < 2$. The simulations show that the mean number of distinct sites visited, $S_n$, varies as

$$S_n = a n^{d_s/2} \tag{98}$$

The decay law for trapping agrees fairly well with $\Phi_n = \exp(-S_n)$ in all the simulations. In most cases, the second approximation was found to be slightly better, but the convergence is slow.

These same authors [63] have simulated the CTRW on fractals. Recall that the waiting time distribution can be of two kinds: having finite mean jump time $\tau_1$ and having infinite $\tau_1$. The case of finite $\tau_1$ is much like the above case of fixed waiting times. However, for infinte $\tau_1$ distributions, such as

$$\psi(t) \sim 1/t^{1+\gamma} \qquad 0 < \gamma < 1 \tag{99}$$

This leads to [63] a form for S(t), see eq. (76b),

$$S(t) \sim t^{\gamma d_s/2} \qquad \text{for } d_s < 2 \tag{100a}$$

and

$$S(t) \sim t^{\gamma} \qquad \text{for } d_s > 2 \tag{100b}$$

(Note that the spectral dimension, $d_s$, comes into play in this dynamics, while in the donor-acceptor case only the fractal dimension, $\bar{d}$, enters.) Eq. (100) show that the two exponents $\gamma$ and $d_s$ combine in a multiplicative manner (subordination).

These same authors [63] have also simulated the problem of trapping on fractals under CTRW dynamics and find

$$\Phi(t) \sim t^{-\gamma}/(c^{2/d_s}) \sim S(t)^{-2/d_s} \qquad \text{for } d_s < 2 \tag{101a}$$

$$\sim t^{-\gamma}/c \sim S(t)^{-1} \qquad \text{for } d_s > 2 \tag{101b}$$

where c is the concentration of traps.

Finally, these authors [63] have simulated the bimolecular reactions mentioned above (Eq. (79)) on fractals (Sierpinski gaskets) and find the decay is well approximated by

$$\phi_n^{AA}(t) = (1+2c\ S_n)^{-1} \tag{102}$$

as in Eq. (80). The reaction $A + B \rightarrow 0$ (with $A_o = B_o$) again is anomalous because of the spatial fluctuations, as mentioned above. Here the decay, $\phi_n^{AB}$ varies as $n^{-d_s/4}$ for $d_s < 4$.

## VI. CONCLUSIONS

We have discussed a number of dynamical processes such as energy transfer, trapping, and optical line shapes in molecular systems, all of which are profoundly affected by the presence of disorder. One of the results of this is a rich variety of time dependencies. For example, disorder can give rise to algebraic decays,

$$\phi(t) \sim \exp t^{-\alpha} \quad ,$$

stretched exponentials,

$$\phi(t) \sim \exp-(t/\tau)^{\alpha}$$

and exponential log decays,

$$\phi(t) \sim \exp-[\ell n^{\alpha}(t/\tau)].$$

Although these time dependencies are associated with disorder, it is often very difficult to uncover the underlying mechanism from the experimental results.

Optical line shapes are also profoundly affected by disorder, becoming broad and featureless. In some cases, however, it is possible to uncover the mechanism of scattering by careful experiment. However, there is still ambiguity in many cases, in particular in the study of optical lines in glasses.

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