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Time-dependent spectral transport: A Monte Carlo study

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An inhomogeneously broadened spectral line, for a spatially random site distribution with dipole-dipole coupling to first-neighbor sites, is studied using a Monte Carlo Technique. The site-site coupling is chosen at random according to the probability density function for first-neighbor dipolar interactions $[\exp(-1/X^{1/2})]/X^{3/2}$; where X is the transfer rate proportional to $1/r^6$, and r is the spatial separation of the interacting sites. This form is appropriate for a dilute concentration of sites on a three-dimensional random lattice. We arrange the sites in a linear array, and the spectral diffusion equation (including back transfer) is solved iteratively. We show that this is an adequate description of the three dimensional system at short and intermediate times for the dilute concentrations considered in this study. A group of sites with a specific energy is excited at (time) $t = 0$. The time development of the excitation profile is then studied. For very short times, the decay of the initial excitation is linear in time, appropriate to the largest value of X (near neighbor site). For longer times, but over a fairly narrow time interval, the decay proceeds as $\exp(-at^{1/2})$, as calculated by Inokuti and Hirayama for dipolar coupling in the absence of back transfer. At the longest times, the decay follows the one-dimensional diffusion result, $t^{-1/2}$. The intermediate-time regime, covering most of the decay of the initial excitation profile, does not seem to follow any simple time dependence.

I. INTRODUCTION

We have considered the physics of spectral diffusion for inhomogeneously broadened spectral lines in a previous publication.[1] We examined several frequency shifting mechanisms, involving inelastic phonon scattering in order to make up the energy mismatch between spatially separated sites. These processes could be grouped into two categories—those which did, and those which did not, depending on the energy mismatch between the initial and final sites. We solved for the time development of the emission profile for both cases, and for Lorentzian and Gaussian inhomogeneous line profiles. Our approach focused on the energy shifting property of the inelastic phonon scattering, and we used an average for the site-site coupling strength in the time development calculations.

It is clear, however, that site-site coupling strengths will vary substantially in a randomly occupied lattice. We examine the effect of dispersion in coupling strengths for a dipole-dipole transfer Hamiltonian in this paper. We treat transfer processes independent of energy, and we make the reasonable assumption (for dilute occupancy) that the spatial transfer is dominated by first-neighbor coupling. We compute the time evolution of the excitation profile according to these assumptions.

No analytic solution to this problem exists, and we have resorted to a numerical Monte Carlo approach. This enables us to examine the applicability of a variety of short- and long-time approximations which can be found in the literature. It also serves as a test for future analytic approaches, especially in the intermediate-time regime where no approximate scheme as yet can fully describe the time development. Our approach is as follows. We imagine that a three-dimensional crystal is occupied randomly with sites interacting according to the dipolar interaction (falling off as $1/r^6$ where r is the distance between sites, and is a random variable in this problem). Because the occupancy is considered to be dilute, we assume that the transfer process is dominated by the first neighbor seen by each site. The probability density for the transfer rate between first neighbor sites is then given by $[\exp(-1/X^{1/2})]/X^{3/2}$, where X is proportional to $1/r^6$. In fact, this procedure ignores correlations between bonds (two in our case—see below). However, this does not cause serious error for this probability density.

We arrange the sites in a linear array. The calculation we actually perform thereby appears one-dimensional. In fact, it applies to three dimensions for short and intermediate times, for low densities of active atoms. It fails to exhibit three-dimensional character only at long times. Our argument goes as follows. A one-dimensional description would be justified if only the two nearest neighbors of each active atom played a role in the diffusion process and closed loops were unimportant. We want to show that this is in fact the case for most of the experimentally relevant time regimes for dilute systems.

We first note that, from purely dimensional considerations, there are two time scales in the problem: a short time determined by the distance of closest approach τ_1 and a longer time, τ_2 $(\simeq c^{-2}\tau_1$

for dipolar site-site couplings, where c is the atomic concentration), determined by the average separation of active atoms. The long-time behavior must certainly be a universal function of t/τ_2. This means that the density of active sites on the lattice enters in two qualitatively different ways. It determines the long-time scale, and also the manner in which the universal long-time behavior is approached.

We now establish the above arguments in detail. Consider the time evolution of the system up to some time t. Two types of processes are involved. For those sites connected by small transfer rates W, such that $Wt \ll 1$, there has been only scattering-out processes (no "back flow"), and the geometry of the lattice does not enter (since our probability density for W already takes three-dimensional site occupancy probabilities into account). The contribution to the diffusion of excitation by sites with first neighbors in this category is adequately described by the distribution of near neighbors, and therefore by the one-dimensional array. We note that this type of contribution disappears when $t \simeq \tau_2$.

The contribution of the large transfer rates is more delicate. For these W, $Wt > 1$. In the spirit of a critical path analysis, we consider the lattice formed by connecting sites coupled with these large W. This associates a connected volume $V = (t/\tau_1)^{1/2} a^3$ with each site for dipolar site-site coupling, where a is a lattice constant. Thus, the connected volume fraction is $p = cV/a^3 = c(t/\tau_1)^{1/2}$. This should be compared with the critical volume fraction for percolation,[2] $p_c \simeq 0.15$. For $p < p_c$, one is dealing with an open disconnected network which should be well described by the one-dimensional model. Actually, even this condition is probably too stringent. The density of branching points on the strongly coupled network is only $c/(1-c)$, so that they are still relatively unimportant when $p = p_c$. Most excitations need considerably longer times before they reach a branching point, thereby departing from one-dimensional character. We also note that p is the total fraction of active atoms involved in the large coupling network. Thus, when $p = p_c$, and $t/\tau_1 = (p_c/c)^2$, there are not many of these strongly coupled sites, so that their contribution to the observed decay is necessarily fairly small—certainly smaller than a fraction p_c of the initial amplitude.

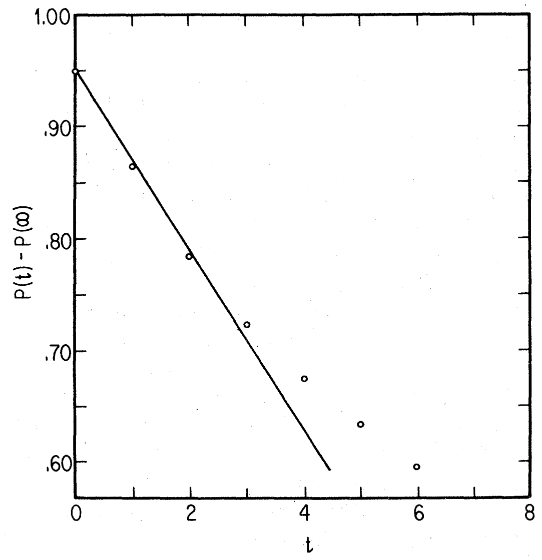

FIG. 1. Plot of $P(E_i, \vec{r}_i, t=\infty)$ vs time (in units of δt) for very short times. $P(E_i, \vec{r}_i, t)$ is the excitation probability of those sites initially ($t=0$) excited with unit probability. The points are the Monte Carlo averaged values (see text).

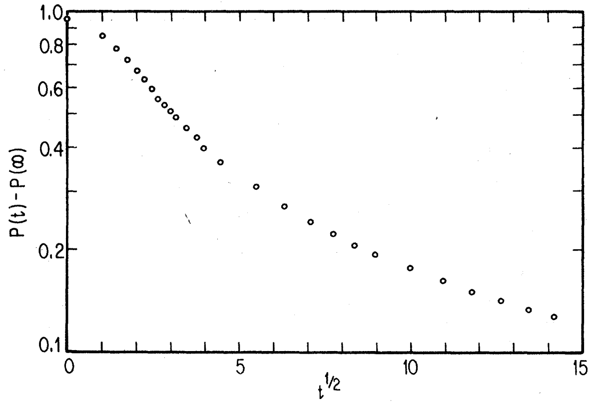

FIG. 2. Semilog plot of $P(E_i, \vec{r}_i, t) - P(E_i, \vec{r}_i, \infty)$ vs $t^{1/2}$.

We conclude, therefore, that the one-dimensional array is a good description of three-dimension-

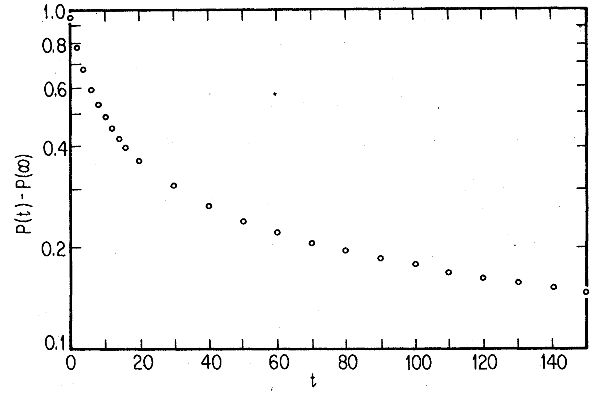

FIG. 3. Semilog plot of $P(E_i, \vec{r}_i, t) - P(E_i, \vec{r}_i, \infty)$ vs t.

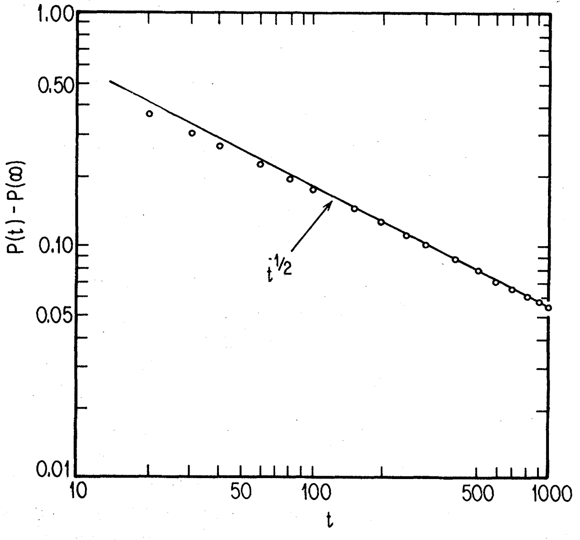

FIG. 4. Log-log splot of $P(E_i, \vec{r}_i, t) - P(E_i, \vec{r}_i, \infty)$ vs t for long times.

al behavior, certainly for $t < t_1$, and quite probably reasonable for times as long as $t < \tau_2$. Near τ_2, the system crosses over to the proper universal three-dimensional behavior, and our one-dimensional array would not be expected to be relevant.

Explicitly, anticipating the results of Sec. II, our model gives $W_{nn} = 0.08 = 1/\tau_1$ in units appropriate to Figs. 1–4. Hence, our model would certainly be an appropriate representation of the three-dimensional situation when $t < \tau_1 = 12(p_c/c)^2$. For a concentration $c = 11\%$, this means that for times less than 22 units the linear array certainly exhibits the behavior of a three-dimensional system. As shown above, this is a very conservative estimate. The particular concentration of 11% is appropriate to our calculation for reasons to be discussed in the next section.

We outline our treatment in Sec. II, and our results are presented and discussed in Sec. III, where the significance of the time interval arrived at above for three-dimensional behavior will be discussed.

II. METHOD OF ANALYSIS

The linear equation for the time development of $P(E_i, \vec{r}_i, t)$, the probability that site $\vec{r}_i$, with energy E_i, is excited at time t, is given by[3]

$$\frac{dP(E_i, \vec{r}_i, t)}{dt} = \sum_j \left[W_{j\to i} P(E_j, \vec{r}_j, t) - W_{i\to j} P(E_i, \vec{r}_i, t) \right]. \qquad (1)$$

The quantities $W_{i\to j}$ are the transfer rates, independent of time, but dependent in general on E_i, E_j, $\vec{r}_i$, and $\vec{r}_j$. We shall assume that the energies E_i span a range less than $k_B T$, so that $W_{i\to j} = W_{j\to i}$. We adopt a dipole-dipole coupling model for W, so that $W_{i\to j} = CX_{ij}$, where C is a constant, and $X_{ij} = 1/|\vec{r}_i - \vec{r}_j|^6$. We ignore any energy dependence for $W_{i\to j}$. This is a correct description for the energy transfer process which varies as T^3_1 involving phonon absorption and emission on sites i and j, respectively.[4] With all these assumptions, (1) reduces to

$$\frac{dP(E_i, \vec{r}_i, t)}{dt} = C \sum_j X_{ij} [P(E_j, \vec{r}_j, t) - P(E_i, \vec{r}_i, t)]. \qquad (2)$$

There is no simple method for solving this equation in random systems. We approach the problem by noting that, for a very dilute system, the overwhelming probability for transfer is between a site and its first neighbor (at the distance $|\vec{r}_{ij}|$). The probability distribution for first neighbors to be coupled with strength CX_{ij} in a three-dimensional crystal is

$$P(X_{ij}) = c[\exp(-a/X_{ij}^{1/2})]/(X_{ij}^{3/2}), \qquad (3)$$

where c and a are constants. We next arrange the sites in one dimension, with the value of X_{ij} between neighboring sites i and j chosen according to (3). This structure will exhibit behavior appropriate to three dimensions in the short- and intermediate-time domain, where the development depends on the density of bond strengths which would enter into such a procedure for a three-dimensional coupling according to (3). In the long-time limit, however, we shall find a diffusion result characteristic of only one dimension $P(E_i, \vec{r}_i, t) \propto t^{-1/2}$.

Using (3), we select transfer rates between neighboring sites for a linear array of 415 sites. We relate the $P(E_i, \vec{r}_i, t)$ to the optical emission probability of a site at $\vec{r}_i$ with emission energy E_i, so that (2) corresponds to the time development of the emission profile and $W_{i\to j}$ to spectral diffusion. We randomly assign energies E_i to the sites, according to a Gaussian probability distribution. For energy independent $W_{i\to j}$, this amounts to nothing more than an accounting procedure. Nevertheless, this random assignment was repeated each iteration. We divide the Gaussian distribution into 41 bins. The Gaussian is centered on the 20th bin. There are 21 sites with this energy, and the remaining sites are assigned energies according to a relative frequency given by the Gaussian probability density. The 21 sites at the center of the distribution are excited at $t = 0$ with unit probability. When the excitations are uniformly distributed amongst all 415 sites (equilibrium), this leads to a $P = 0.05$.

The X_{ij} were distributed according to (3) with

$a = 9.5$, and the distribution cutoff at $X_{ij} = 100$. This choice of a means the distribution peaks at $X_{ij} = 10$. If we interpret the cutoff as that value of X_{ij} appropriate to a near-neighbor distance in a simple cubic lattice, and the peak of the probability distributions situated at the average value of the site separation, this cutoff means an effective site occupancy concentration of $10^{-1/2} = 31.6\%$. A larger value for the cutoff would diminish the effective site concentration, but the slowness of the square-root falloff makes appreciable numerical improvement prohibitively expensive. However, in practice, near-neighbor sites interact so strongly as to be shifted outside of the inhomogeneous line shape. Hence, a physical situation would probably limit one to no closer contact than second near neighbors. This has the effect of enhancing the cutoff (when measured in terms of the lattice constant) and would, for example, result in an 11% effective concentration for the parameters we have used.

The probability distribution for the transition rate [Eq. (3)] was divided into 100 bins, with $P(X_{ij})$ evaluated at the center of the bin ($X_{ij} = 0.5$, 1.5, etc.). The same method was used here as in the assignment of energies. There are ten bonds with $X_{ij} = 10$, while the remaining bonds are assigned according to the probability density function (3). Equation (2) was iterated numerically according to the Euler method

$$P(E_i)_{t_0+\delta t} = P(E_i)_{t_0} + \delta t \sum_{j=1}^{415} [W(j \to i)P(E_j)_{t_0} - W(i \to j)P(E_i)_{t_0}], \quad (4)$$

for $i = 1, 2, \ldots, 415$. The indices i and j correspond to the ith and jth sites and the W are chosen according to (3). For the problem at hand, $W(j \to i) = W(i \to j)$ (see Ref. 1). The $P(E_i)$ are distributed amongst the 41 bins according to the Gaussian probability density described above. Choosing the constant $C = 1.27 \times 10^{-4}$ in (2) allowed for δt as large as 10 without divergent behavior.

The 414 bonds were assigned randomly and the iteration [Eq. (4)] was carried out over 1000 cycles. The initial site amplitudes decayed by this time to within 0.056 of their equilibrium value (0.05) from their initial value of unity. This amplitude change corresponds very roughly to the time interval over which most spectral transfer experiments have been performed. The entire procedure was repeated a total of ten times, with new random coupling assignments being made according to (3) each time. The respective profiles were averaged at a given time, and the results displayed over the full time interval. A short-time (20 cycles) iteration was repeated twenty times, with results identical to the (long-time) repetition of ten times, suggesting our Monte Carlo procedure was adequate.

The results are exhibited and discussed below.

III. RESULTS AND CONCLUSIONS

Four graphs are sufficient to understand the physics of our results. Figure 1 displays the excitation amplitude of the initially excited sites (less the equilibrium value) vs. time (in units of the time increment δt) on a linear plot; Fig. 2 on a semilog plot vs. $t^{1/2}$, Fig. 3 on a semilog plot vs. t; and Fig. 4 on a log-log plot. The time ranges are different, for reasons to be discussed below.

The full emission profile (for all 415 sites) develops as expected for energy mismatch independent $W_{i\to j}$. The initially excited sites decay according to Figs. 1–4, while their intensity is transmitted to the full background line shape without distortion, the total excitation probability being conserved.

We now examine the signifance of our results.

A. Very short-time behavior

In the vicinity of $t = 0$, the cutoff in $W_{i\to j}$ manifests itself by a linear time dependence of $P(E_i, \vec{r}_i, t)$.[5] In a physical system, this is the result of neighboring sites for which the initial transfer is made at the rate given by the cutoff in our model (the maximum rate). Our results exhibit this behavior in Fig. 1, but only for $0 < t < 3$, or, more usefully, for $P(E_i, \vec{r}_i, t)$ falling to about three-quarters of its initial value.

B. Short-time behavior

A glance at Fig. 2 shows that $P(E_i, \vec{r}_i, t) \propto \exp(-t^{1/2})$, the scattering out only prediction for dipole-dipole coupling of Inokuti and Hiryama,[6] for $3 \lesssim t \lesssim 10$. This corresponds to $P(E_i, \vec{r}_i, t)$ varying between about 0.75 to 0.5 of its initial value, even for such a short-time regime. The fact that this behavior is exhibited for a narrow time interval is caused by the relatively high concentration appropriate to our cutoff of the distribution for $W_{i\to j}$ [Eq. (3)]. Had we increased the cutoff, the early time boundary on the simple scattering out theory would have been pushed back towards $t = 0$. Our results suggest that only for concentrations in the vicinity of, or less than, a few percent can one expect the Inokuti-Hiryama result to hold over the full early time period.

C. Intermediate-time behavior

One would expect scattering in, the first term on the right-hand side of (1) and (2), to become important when $P(E_i, \vec{r}_i, t) \sim 0.5$. Indeed, this is observed to be the amplitude at which $P(E_i, \vec{r}_i, t)$ breaks away from the Inokuti-Hiryama form on Fig. 2. We plot the full time dependence on Fig. 3. The intermediate time behavior spans the region between $t = 10$ and $t = 100$, beyond which diffusion takes over (see below). This means that scattering in, and nondiffusive behavior, are significant for $0.5 \gtrsim P(E_i, \vec{r}_i, t) \gtrsim 0.2$. There are no analytic forms for the predicted decay of P in this regime. Huber *et al.*[5] have experimented with a variety of approximations, but they fail in the longer time regime. Strictly speaking, the results of our calculation fail to exhibit behavior appropriate to three dimensions in this time regime (see Introduction). For times beyond 22 units, a small fraction of the sites are connected beyond the critical volume fraction threshold, and our one-dimensional array may no longer be a valid representation of three-dimensional behavior. This means that our numerical results have a direct relationship to three dimensions only in regimes A and B, and for the early part of C, though as shown in the Introduction this restriction may be overly conservative.

D. Long-time behavior

When $P(E_i, \vec{r}_i, t) \lesssim 0.2$ of its original value, diffusion appears to be dominant. The actual time domain over which diffusion becomes effective is dependent on the character of $P(X_{ij})$.[7] For the dipolar case, one-dimensional diffusion behavior, $P(E_i, \vec{r}_i, t) \sim t^{-1/2}$, holds for all times greater than 100 units (see Fig. 4). A fit to the "data" over this time domain yields

$$P(t) - P(\infty) = 5.69 t^{-1/2} . \qquad (5)$$

It turns out that the long-time limit is calculable exactly for one dimension. Bernasconi[8] finds

$$P(t) - P(\infty) = [1/(4\pi W_{\text{eff}})^{1/2}]\, t^{-1/2} \;, \qquad (5')$$

where $1/W_{\text{eff}} = \langle 1/W_{i\to j} \rangle$, the ensemble average of the transition rates. Equation (5) leads to $W_{\text{eff}} = CX_{\text{eff}} = 2.46 \times 10^{-3}$. Using our value for C, $X_{\text{eff}} = 19.35$. Bernasconi's expression[8] for X_{eff} is

$$\frac{1}{X_{\text{eff}}} = \int_0^{100} dx\, x^{-5/2} e^{-a/x^{1/2}} \times \left(\int_0^{100} dx\, x^{-3/2} e^{-a/x^{1/2}} \right)^{-1} = 18.8^{-1} , \qquad (6)$$

for $a = 9.49$, as taken in this paper. The agreement is excellent, well within the fitting error to the Monte Carlo results.

One might be tempted to accept the diffusion form for the long-time limit of $P(E_i, \vec{r}_i, t)$ as a general result. However, as stressed in Refs. 7 and 8, even the one-dimensional $(t^{-1/2})$ behavior is not a trivial result for disordered systems, and in fact is only true for a certain class of probability distributions for $W_{i\to j}$ [of which, it turns out, (3) is a member]. Therefore, though the Monte Carlo results for dipolar interactions do generate diffusion behavior at long times, the more general case is by no means trivial, and a full solution for three dimensions remains inaccessible at present.[9]

In conclusion, we have examined the time development of the emission profile for energy independent transfer rates in a random system. We have assumed dipolar coupling between sites and included only first-neighbor interactions according to the distribution law

$$P(X) = \exp(-a/X^{1/2})/X^{3/2},$$

$$X = 1/r^6 .$$

The time development equations were solved iteratively for a random selection of transfer rates between sites successively coupled (a linear array). The very-short-time behavior exhibited a linear dependence on t, caused by the introduction of a (maximum) cutoff on the transition rate (relating to a finite distance of closest approach). The scattering out only solution dominates in the next time interval, failing when the probability amplitudes fall to 50% of their initial values. Scattering in then becomes important, and no simple solution exists for the time development. Finally, diffusion characterizes the very long-time behavior, for excitation amplitudes less than 20% of their initial values.

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$$P(W_{i-j}) = p\delta(W_{i-j}) + (1-p)\,\delta(W_{i-j} - W_0).$$

For $p > 0.2$, there may be *no* time regime where diffusion is significant.

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