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A Theory of Exciton Dynamics with a Percolation Threshold

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Mode-coupling methods are used to obtain an integral equation for the exciton diffusion constant in isotopically mixed crystals. Numerical solutions are obtained for nearest neighbor hopping in one- and two-dimensional square lattices. These solutions exhibit percolation thresholds.

KEY WORDS: Exciton; master equation; mode coupling; percolation.

1. INTRODUCTION

The concept of percolation$^{(1)}$ has been successfully applied$^{(2)}$ to the problem of exciton migration in isotopically mixed crystals. A crystal is prepared containing exciton conductors, exciton insulators, and, optionally, a very low concentration of energy traps or sensors.

As the conductor concentration is raised, a critical concentration is reached$^{(2)}$ at which exciton migration becomes very much more efficient. This concentration can be$^{(2)}$ interpreted as the percolation threshold for formation of an infinite cluster of conductors, with the definition of connectedness being appropriate for whatever the range of the conductor–conductor interaction might be.

Given that percolation is an important concept for exciton migration, an obvious question is: can we construct a careful quantitative theory of exciton dynamics which naturally includes the consequences of percolation? The mathematical definition$^{(1)}$ of percolation is purely static, while exciton migration is inherently dynamic, so the problem is by no means trivial.

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Kopelman et al.$^{(2c)}$ have made some progress in this area by, in brief, assuming a knowledge of the static problem and then considering the dynamics of each sized cluster separately, with an eventual average over the distribution of cluster sizes. Blumen and Silbey$^{(2d)}$ have presented a successful, phenomenological theory. We have also$^{(2e)}$ addressed the question via a computer simulation. However, a dynamical theory which shows a percolation threshold that has not already been built in—a completely self contained theory—has not been given so far. We present such a theory in this paper.

2. MASTER EQUATION

We shall treat a crystal with conductors, insulators, and no sensors. For low sensor concentrations, the energy which will register at a sensor can be calculated from the problem we solve. For a given configuration (assignment of conductors and insulators to lattice sites) of the crystal, we assume that energy migration among the conductors is described by a simple master equation,

$$\dot{E}_i = -\left(\sum_j T_{ij}\right)E_i(t) + \sum_j T_{ji}E_j(t) \tag{1}$$

$E_i(t)$ is the energy of conductor i at time t, and $T_{ij} = T_{ji} = T(|\mathbf{r}_{ij}|)$, where T is the distance-dependent hopping probability and $\mathbf{r}_{ij}$ is the separation of conductors i and j. Equation (1) must be solved for each configuration and averaged over configurations to obtain the macroscopic properties of exciton migration; the average is denoted by $\langle\ \rangle$.

Equation (1) is usefully rewritten by the introduction of the occupation numbers, ϵ_s:

$$\begin{aligned} \epsilon_s &= 1, \quad \text{site } s \text{ occupied by conductor} \\ &= 0, \quad \text{otherwise} \end{aligned} \tag{2}$$

Then

$$\dot{E}_s(t) = -\sum_{s'}\left[\epsilon_{s'}T_{s,s'}E_s(t) - \epsilon_s T_{s,s'}E_{s'}(t)\right] \tag{3}$$

where the sum is over the entire lattice.

It will be necessary to develop approximate solutions of Eq. (3), so we make the following observation. In a perfect crystal of conductors, there are no conductor concentration fluctuations. In a nearly perfect crystal the conductor concentration fluctuations are very small compared to those in a noninteracting lattice gas of conductors, and an expansion in these fluctuations is appropriate. Our theory is based upon a fluctuation expansion and thus is designed to describe the high density regime, approaching the percolation threshold from above.

Writing $\epsilon_s = \langle\epsilon\rangle + \delta\epsilon_s$, where $\langle\epsilon\rangle$ is the conductor fraction, a dimensionless measure of conductor concentration which lies between zero and one, Eq. (3) becomes

$$\dot{E}_s(t) = -\sum_{s'} K_{s,s'} E_s(t) - \sum_{s'} T_{s,s'}\left[E_s(t)\delta\epsilon_{s'} - E_{s'}(t)\delta\epsilon_s\right] \tag{4}$$

where K is a kernel which does not depend on the configuration,

$$K_{s,s'} = \langle\epsilon\rangle\left(\delta_{s,s'}\sum_{s'} T_{s,s'} - T_{s,s'}\right) \tag{5}$$

and $\delta_{s,s'}$ is a Kronecker delta; Note $\sum_{s'} T_{s,s'}$ is not a function of s. Thus, Eq. (4) separates the exciton dynamics into a "mean field" part and a concentration (occupation number) fluctuation part.

Equation (4) is of a much studied form—it has a quadratic nonlinearity—and may be solved and averaged using the methods[(3)] of mode coupling theory. Interestingly, Eq. (4) may be uniquely amenable to mode coupling analysis. Usually, the quadratic term is a product of two independent, time-dependent variables. Here, however, $\delta\epsilon_s$ is a time-independent constant for each configuration, and the time-dependent $E(t)$ is determined by $\delta\epsilon$. The result, to which we proceed now, is the simplest mode coupling problem we have ever seen.

3. SOLUTION AND AVERAGING

Following Kawasaki[(3a)] we first Fourier–LaPlace-transform Eq. (4); we use the lattice version of the Fourier transform,

$$E_{\mathbf{k}} = \sum_{s} \exp(i\mathbf{k}\cdot\mathbf{s})E_s \tag{6a}$$

where we write $\mathbf{s}$ instead of $\mathbf{r}_s$, with the inverse,

$$E_s = \frac{1}{(2\pi)}3\,\frac{1}{v}\int_{\mathrm{Bz}} d\mathbf{k}\exp(-i\mathbf{k}\cdot\mathbf{s})E_{\mathbf{k}} \tag{6b}$$

where v is the volume of the Brillouin Zone, and $\int_{\mathrm{Bz}}$ is an integral over the Brillouin zone. Thus,

$$(z + K_{\mathbf{k}})E_{\mathbf{k}}(z) = E_{\mathbf{k}}(t=0) + \frac{1}{(2\pi)^3 v}\int_{\mathrm{Bz}} d\mathbf{k}'\left[T_{\mathbf{k}+\mathbf{k}'}\delta\epsilon_{-\mathbf{k}'} - T_{-\mathbf{k}'}\delta\epsilon_{-\mathbf{k}'}\right]E_{\mathbf{k}+\mathbf{k}'} \tag{7}$$

and the wave vector mixing or "mode coupling" character of the second term on the right of Eq. (7) is apparent. It is clear from Eq. (5) that $K_{\mathbf{k}}$

varies as k^2 for small k, so let

$$K_{\mathbf{k}} \equiv k^2 D^0_{\mathbf{k}} \tag{8}$$

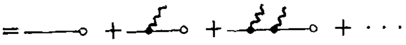
in the absence of concentration fluctuations exciton migration is diffusive with diffusion constant D^0.

We will now proceed to calculate an exciton diffusion constant which includes the effects of fluctuations as well. The calculation is almost identical to the mode coupling discussed in great detail in Ref. 3, so we only give an outline here; a reading of Ref. 3 should answer any resulting questions.

A formal solution of Eq. (7) may be compactly represented(3) graphically. With the following definitions and correspondences,

$$\begin{aligned} E_{\mathbf{k}}(t=0) &= \bigcirc \\ W_{\mathbf{k},\mathbf{k}'} = T_{k+k'} - T_{-k'} &= \bullet \\ \delta\epsilon_{-\mathbf{k}'} &= \sim\!\sim\!\sim \\ G^0_{\mathbf{k}}(z) = \left(z + k^2 D^0_{\mathbf{k}}\right)^{-1} &= \text{——} \end{aligned} \tag{9}$$

we may write the result of iterating Eq. (7) as

$E_{\mathbf{k}}(z) =$  (10)

Each line is assigned a wave vector subject to the rule that the wave vector emerging from the left of a vertex (W) is equal to the sum of the two wave vectors of the lines which entered on the right, and the wave vector of the leftmost line is **k**. An integral, $[1/(2\pi)^3 v]\int_{\mathrm{Bz}}$, is performed over all intermediate wave vectors.

Although this is not a paper on mode coupling theory, it seems worth pointing out, for those familiar with the field, that the graphs in Eq. (10) are extremely simple. Their general form is a line with wiggly lines attached at multiple points, and no more complicated branching occurs; this is a consequence of only one of the variables in the bilinear term being time dependent. For that same reason, averaging Eq. (10) will not introduce time-dependent correlation functions, also a major simplification with respect to the usual(3) case.

We now average Eq. (10) over the concentration or occupation number fluctuations, which will generate multipoint, same-time correlation functions of $\delta\epsilon$. To keep the problem tractable, we now introduce, as usual, a Gaussian approximation; higher-order correlation functions are written as all products of pair correlation functions. Since the only nonzero pair correlation functions are of form $\langle \delta\epsilon_{k'} \delta\epsilon_{-k'} \rangle$, the wave vectors are paired correspondingly. Graphically, a pairing is denoted by joining the two appropriate wiggly lines, which then represent a pair correlation function.

Although we have been stressing the simplicity of the present problem, one complication exists as well. In contrast to the usual case, it is unphysical for us to regard $E_{\mathbf{k}}(t = 0)$ as under experimental control and independent of the configuration. The experiments can only control the spatial distribution of the exciting radiation, $I(\mathbf{r})$, and

$$E_{\mathbf{k}}(t = 0) = \frac{A}{(2\pi)^3 \nu} \int_{\mathrm{Bz}} I_{\mathbf{k}+\mathbf{k}'} \epsilon_{-\mathbf{k}'} \, d\mathbf{k}' \tag{11}$$

where A is a constant of no interest here; energy can be initially present only at conducting sites, so E_k and ϵ are intimately linked.

Two initial intensities naturally suggest themselves for a calculation of the exciton diffusion constant at wave vector $\mathbf{k}$. First, the initial intensity might also be characterized by wave vector $\mathbf{k}$,

$$I_q = \mathrm{const} \times \delta(\mathbf{q} - \mathbf{k})$$

in which case Eq. (11) becomes

$$E_{\mathbf{k}}(t = 0) \propto \frac{1}{(2\pi)^3 \nu} \int_{\mathrm{Bz}} d\mathbf{k}' \, \delta(k') \epsilon_{-k'}$$

Now, corresponding to the division of ϵ_s into the average and a fluctuation,

$$\epsilon_{\mathbf{k}} = (2\pi)^3 \nu \langle \epsilon \rangle \delta(\mathbf{k}) + \delta\epsilon_{\mathbf{k}} \tag{12}$$

so, in this case,

$$E_{\mathbf{k}}(t = 0) \propto \langle \epsilon \rangle$$

$\delta\epsilon_0$ being negligible compared to the delta function. Thus, the initial condition is independent of configuration, and $E_{\mathbf{k}}(t; I_{\mathbf{k}})$ may be calculated as usual, i.e., with an assumed knowledge of $E_{\mathbf{k}}$ $(t = 0)$.

Alternatively consider an initial intensity localized on one site, which facilitates thinking about an exciton "random walking" around the crystal. Then $I_{\mathbf{k}} = \mathrm{const}$, and

$$E_{\mathbf{k}}(t = 0) \propto \int_{\mathrm{Bz}} d\mathbf{k}' \, E_{-k'} = \nu (2\pi)^3 \langle \epsilon \rangle + \int_{\mathrm{Bz}} d\mathbf{k}' \, \delta\epsilon_{-k'} \tag{13}$$

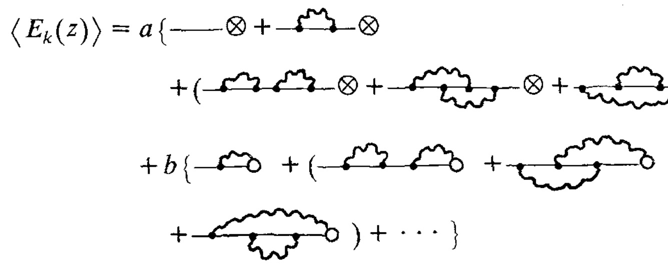
Thus, the initial condition now has one part which is independent of the configuration but one part which depends on the configuration, a new feature. Let us make a graphical representation of a general initial condition

$$0 = a \otimes + b0^{\rightsquigarrow} \tag{14}$$

with the first term (a) representing the nonfluctuating part and the second term (b) depending on $\delta\epsilon$; b can be zero. It is easy to see that the configuration-independent part of the initial condition is just its average, so

$$a \otimes \leftrightarrow \langle E_{\mathbf{k}}(t=0)\rangle \tag{15}$$

We may now average by pairing up the wiggly lines in the graphs, the result being(3)



(16)

Graphs proportional to a have an even number of vertices and are the usual mode coupling graphs, while the b graphs have an odd number of vertices and are new, with the fluctuation initial condition playing the role of an extra vertex.

Some of the graphs in Eq. (16) can be separated into disconnected parts by cutting a single $G_{\mathbf{k}}^0$ line. These graphs are, as usual, expressed in terms of graphs ("connected graphs") which cannot be so disconnected via introduction of the self energy, $\sum_{\mathbf{k}}(z)$, the result being

$$\langle E_{\mathbf{k}}(z)\rangle = \left[\left(G_{\mathbf{k}}^0(z)\right)^{-1} + \textstyle\sum_{\mathbf{k}}(z)\right]^{-1}\left[\langle E_{\mathbf{k}}(t=0)\rangle + b\Delta_{\mathbf{k}}(z)\right] \tag{17}$$

and we define the full propagator, G,

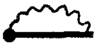
$$\text{———} = G_{\mathbf{k}}(z) = \left\{\left[G_{\mathbf{k}}^0(z)\right]^{-1} + \textstyle\sum_{\mathbf{k}}(z)\right\}^{-1} \tag{18}$$

$\sum$ is the sum of all graphs generated from the connected graphs in the a series by removing — from the left and —$\otimes$ from the right. The new feature in Eq. (17) is the initial condition fluctuation term, $b\Delta_{\mathbf{k}}$, which is the sum of all graphs obtained from the b series by splitting off as much of the left-hand side of the graph as is possible by cutting a single G^0 line and erasing its fragments; the result is a connected graph with a vertex on the left which contains 0. The first few graphs in $b\Delta$ are given by

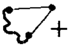
(19)

G is the same propagator that appears in the absence of the "fluctuating initial condition" complication.

Since $\sum$ is expressed in terms of G^0, Eq. (18) gives G in terms G^0. As has been discussed exhaustively elsewhere,$^{(3)}$ it is possible to write a self-consistent, or integral equation for G via introduction of the "renormalized vertex," denoted by a heavy dot, $\bullet$, in which case

$\sum =$  (20)

i.e., $\sum$, and G, are functions of G, not G^0. The first two contributions to $\bullet$ are

$\bullet = \cdot +$  $+ O(W^5)$ (21)

In view of our interest in percolation, it is natural to focus attention on the exciton diffusion constant, $D_{\mathbf{k}}(z)$. With any proper definition of $D_{\mathbf{k}}(z)$, the mean square displacement, $\langle S^2(t)\rangle$, of an exciton originally localized at the origin of coordinates will be given by the relation,

$$\langle S^2(t)\rangle = td \lim_{\substack{k\to 0\\ z\to 0}} D_{\mathbf{k}}(z) \equiv t\,dD \tag{22}$$

at long times, where d is the dimension. Now, below the percolation threshold, the site at which the exciton starts must$^{(1,2)}$ be a member of a finite cluster of conductors. The threshold, of course, is a function of the definition of connectedness. If T_{ij} is identically zero for $r_{ij} > R_c$ and constant for $T_{ij} < R_c$ then R_c is the separation over which two conductors are connected. If T is a smooth function, no straightforward connection to a percolation threshold exists.

For the case that R_c exists, which we discuss in detail later on, $\langle S^2(t)\rangle$ cannot increase as t for arbitrarily large t below the threshold, as $\langle S^2\rangle$ can never be bigger than the square of a dimension of a finite cluster. Thus, D must vanish as the conductor concentration drops below the threshold, and D is clearly an excellent vehicle for the discussion of the role of percolation.

In the absence of a fluctuating initial condition, the appropriate definition is

$$G_{\mathbf{k}}(z) = \left[z + k^2 D_{\mathbf{k}}(z)\right]^{-1} \tag{23}$$

It is easy to see that Eq. (23) is also appropriate for the case at hand. Every graph in $\Delta_{\mathbf{k}}(z)$ has a leftmost vertex with two wave vectors which add to $\mathbf{k}$ entering on the right. So, according to Eq. (9), $\Delta_k(z) \propto ik$ and

$$E_{\mathbf{k}}(z) \simeq G_{\mathbf{k}}(z)\langle E_{\mathbf{k}}(t=0)\rangle, \qquad \text{small } k \tag{24}$$

It follows that if $D_{\mathbf{k}}(z)$ is defined according to Eq. (23), D obeys Eq. (22) and is thus a "proper" D.

In short we have shown that the fluctuating initial condition does not complicate a mode coupling theory for $D_{\mathbf{k}}(z)$. $G_{\mathbf{k}}(z)$ has the usual graphical expansion, and Eq. (23) converts an integral equation for $G_k(z)$ into one for $D_{\mathbf{k}}(z)$, with $\lim_{k\to 0, z\to 0} D_{\mathbf{k}}(z)$ having the usual properties of a diffusion constant; the latter point is only true because $\Delta_{\mathbf{k}} \propto ik$. The presence of $\Delta_{\mathbf{k}}(z)$ may change the physical meaning of $D_{\mathbf{k}}(z)$ for high k from its usual meaning.

3. APPROXIMATE INTEGRAL EQUATION FOR $D_{\mathbf{k}}(z)$

In the current formulation,$^{(3)}$ approximations are made to $\bullet$. We will study the simplest approximation which is almost always used, $\otimes \cong \cdot$. Converting the graphical notation back to reality, and using Eqs. (8), (9), (20), and (23), we find

$$D_{\mathbf{k}}(z) = D_{\mathbf{k}}^0 - \frac{1}{(2\pi)^3} v \int_{\mathrm{Bz}} d\mathbf{k}' \left(W_{\mathbf{k},\mathbf{k}'} W_{\mathbf{k}',\mathbf{k}} k^{-2} \right) \langle \delta\epsilon_{\mathbf{k}'} \delta\epsilon_{-\mathbf{k}'} \rangle$$
$$\times \left[z + k'^2 D_{k'}(z) \right]^{-1} \tag{25}$$

Equation (25) is our basic result, which we will now discuss and solve in some simple cases.

First, note that an equation much like Eq. (25) could have been derived from Eq. (7) by a very simple, if somewhat unsystematic, technique. Immediate averaging of Eq. (7) produces $\langle E_{\mathbf{k}+\mathbf{k}'} \delta\epsilon_{-\mathbf{k}'} \rangle$ as the difficult quantity on the right-hand side. Multiplication of Eq. (7), with $\mathbf{k} \to \mathbf{k} + \mathbf{k}'$, by $\delta\epsilon_{\mathbf{k}'}$, followed by averaging, leads to an equation for $\langle E_{\mathbf{k}+\mathbf{k}} \delta\epsilon_{-\mathbf{k}'} \rangle$ which contains $\langle E_{\mathbf{k}+\mathbf{k}'+\mathbf{k}''} \delta\epsilon_{-\mathbf{k}''} \delta\epsilon_{-\mathbf{k}'} \rangle$ on the right-hand side. If we make a Gaussian approximation, $\langle E_{\mathbf{k}+\mathbf{k}'+\mathbf{k}''} \delta\epsilon_{-\mathbf{k}'} \rangle \simeq \langle E_{\mathbf{k}+\mathbf{k}'+\mathbf{k}''} \rangle \langle \delta\epsilon_{-\mathbf{k}''} \delta\epsilon_{-\mathbf{k}'} \rangle$, where we have noted that $\langle \delta\epsilon \rangle = 0$. The equation for $\langle E_{\mathbf{k}+\mathbf{k}'} \delta\epsilon_{-\mathbf{k}'} \rangle$ can now be solved and substituted into the equation for $\langle E_{\mathbf{k}} \rangle$. The result is almost Eq. (25); the difference is that D^0, and not D, appear in the propagator on the far right. We are not recommending this procedure, but just point it out for whatever insight it can give into Eq. (25).

Turning to the result itself, note that the second term on the right is independent of k as $k \to 0$, as it should be. Because $T_{s,s'}$ only depends on $|s - s'|$, it follows that, for small k,

$$W_{\mathbf{k},\mathbf{k}'} = \text{const} \times \mathbf{k} \cdot \mathbf{k}' + O(k^3)$$
$$W_{\mathbf{k}',\mathbf{k}} = f(|k'|) + \mathbf{k} \cdot \mathbf{k}' g(|k'|) + \cdots$$

These results, combined with the observation that $\langle \delta\epsilon_{\mathbf{k}'} \delta\epsilon_{-\mathbf{k}'} \rangle$ and $D_{\mathbf{k}'}(z)$ only depend on $|k'|$ in a crystal with no unique spatial dimension, to which we confine the discussion, show that the $\mathbf{k}'$ integral produces the desired result as $k \to 0$.

$D_{\mathbf{k}}^0$ is the "mean field" result and lacks any contribution from fluctuations. Its concentration dependence is just $\langle \epsilon \rangle$, zero at zero concentration and unity for a pure conductor crystal. $D_{\mathbf{k}}^0$ contains no thresholds. As the density is decreased, exciton diffusion slows down in a simple way which can be treated by a simple change of timescale.

This behavior of $D_{\mathbf{k}}^0$ makes perfect sense. As discussed earlier, D is expected to vanish below a percolation threshold because an exciton is then trapped on finite "islands," and $\langle S^2(t) \rangle$ cannot keep increasing as t at very large t. Now the presence of "islands" and the presence of concentration fluctuations are the *same thing*! There can be no islands without concentration fluctuations, which D^0 explicitly avoids, so D^0 should not respond to a percolation threshold.

It is possible to imagine a hypothetical system which makes the nature of D^0 very clear. Suppose that for, e.g., $\langle \epsilon \rangle = 0.5$, every site of the lattice was still occupied, but by one-half of a conductor, and so forth. Then no islands would exist. "Half conductors" would have a weaker pair interaction, so diffusion would slow, but in a way corresponding to a timescale change. Such a system is described by D^0.

The integral term in Eq. (25) contains an approximate treatment of fluctuation. The term has three qualitatively correct features:

(i) It is negative, and so reduces D below its mean field value, as it should.

(ii) It is proportional to the mean square conductor fluctuations, $\langle \delta\epsilon_{\mathbf{k}'} \delta\epsilon_{-\mathbf{k}'} \rangle$, and thus vanishes as $\langle \epsilon \rangle \to 1$ (no fluctuations in a perfect crystal).

$\langle \delta\epsilon_{\mathbf{k}'} \delta\epsilon_{-\mathbf{k}'} \rangle$ becomes$^{(4)}$ important at intermediate $\langle \epsilon \rangle$ and also vanishes$^{(4)}$ as $\langle \epsilon \rangle \to 0$, which leads to further physically correct behavior of the fluctuation contribution to D.

(iii) The percolation threshold which enters D is, as discussed, a function of the range over which $T_{s,s'}$ is nonzero. Obviously, an exciton which can only hop short distances can be trapped more easily, with smaller insulator barriers, than a longer range-hopping exciton. This behavior is present in Eq. (25). The interaction range, R_c, enters the W functions. For $k' > R_c^{-1}$, the quantity in the square bracket vanishes and "cuts off" the $\mathbf{k}'$ integral. Thus, D only gets contributions from concentration fluctuations, $\langle \delta\epsilon_{\mathbf{k}'} \delta\epsilon_{-\mathbf{k}'} \rangle$, with $k' \lesssim R_c^{-1}$.

This result makes beautiful sense. Roughly, a fluctuation of wave vector $\mathbf{k}'$ occurs over a spatial dimension of k'^{-1}. In other words a fluctation with $k' < R_c^{-1}$ disrupts the conductor structure over a distance *greater* than the hopping distance, and thus decreases D. Higher k', or shorter distance, fluctuations have no effect on D.

In sum, the approximate theory has many obvious, desirable features. However, an actual solution of the equation is necessary for a real test of the theory; in particular, the qualitative discussion cannot tell us if Eq. (25) yields a D with a percolation threshold.

4. CALCULATION OF D FOR SOME SIMPLE LATTICES; DISCUSSION

We have obtained D by numerical analysis on one-dimensional and two-dimensional square lattices for nearest neighbor hopping,

$$\begin{aligned} T_{s,s'} &= \text{const}, \qquad s,s' \text{ nearest neighbors} \\ &= 0, \qquad \text{otherwise} \end{aligned} \tag{26}$$

and under the assumption that $\langle \delta\epsilon_{k'} \delta\epsilon_{-k'} \rangle$ has the form found in the simplest lattice gas theories,$^{(4)}$

$$\langle \delta\epsilon_{\mathbf{k}'} \delta\epsilon_{-\mathbf{k}'} \rangle = \langle\epsilon\rangle(1 - \langle\epsilon\rangle) \tag{27}$$

use of a more complicated expression for the fluctuations would not complicate the analysis, but we are not interested in refinements of the theory at this point.

For the two-dimensional square lattice with nearest neighbor hopping the percolation threshold is$^{(1)}$ 0.58. One dimension is a pathological case for percolation, with threshold at $\langle\epsilon\rangle = 1$, corresponding to the fact that a single insulator creates "islands" in one dimension. Recall that we have formulated an approximate treatment of the fluctuation contribution to D. So, the greater the importance of fluctuations, the more severe will be the test of our approximation. Very broadly speaking, fluctuations decrease in importance as dimension increases, and our theory should improve as d increases.

We solved Eq. (25) for $z = 0$ by iteration about the mean field result. For $\langle\epsilon\rangle \lesssim 1$, the iteration converges very quickly. As $\langle\epsilon\rangle$ is decreased convergence slows, but the trend of successive iterates remains monotone, decreasing smoothly from D^0. A critical value of $\langle\epsilon\rangle, \langle\epsilon\rangle_c$ is finally reached, defined within the numerical analysis as follows: A further decrease of 0.001 in $\langle\epsilon\rangle$ causes the series of successive D's to oscillate violently, including negative values, with no signs of convergence. Further lowering of $\langle\epsilon\rangle$ worsens the situation.

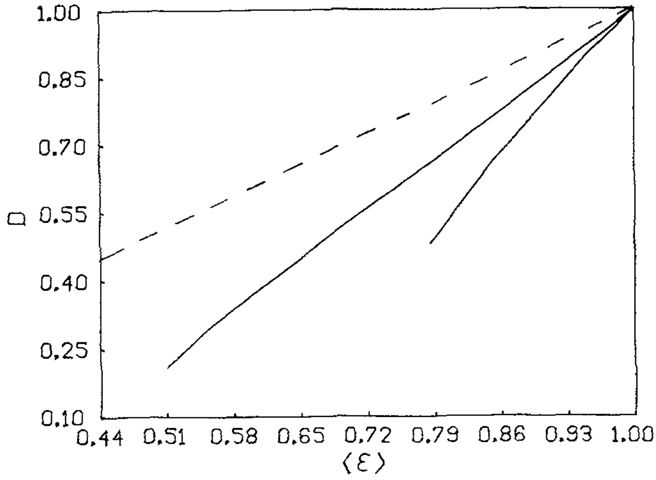


Fig. 1. Plot of the exciton diffusion constant, D, vs. conductor concentration, $\langle\epsilon\rangle$. Lower and middle solid curves are theoretical results for one and two dimensions, respectively; curves terminate at $\langle\epsilon\rangle = \langle\epsilon\rangle_c + 0.005$. Dashed line is mean field D.

It appears, then, that $\langle\epsilon\rangle_c$ gives the radius of covergence of the high density solution generated by the fluctuation expansion. We suggest $\langle\epsilon\rangle_c$ is a percolation threshold.

In Fig. 1, we show the results just discussed, plotting $D(\langle\epsilon\rangle)/D(\langle\epsilon\rangle = 1)$ vs. $\langle\epsilon\rangle$ [recall $D(\langle\epsilon\rangle = 1) = D^0(\langle\epsilon\rangle = 1)$]. $D^0/D(\langle\epsilon\rangle = 1)$ is just a straight line running from 0 at $\langle\epsilon\rangle = 0$ to unity at $\langle\epsilon\rangle = 1$. The $\langle\epsilon\rangle_c$'s we find are 0.505 in two dimensions and 0.78 in one dimension. These answers are not perfect, and may be put in perspective by the relations

$$\begin{aligned}\langle\epsilon\rangle &= 0.87\langle\epsilon\rangle_c^{\text{exact}}, \qquad \text{two dimensions}\\ &= 0.78\langle\epsilon\rangle_c^{\text{exact}}, \qquad \text{one dimension} \qquad (28)\end{aligned}$$

So our percolation thresholds are too low in one and two dimensions, the situation being better in $d = 2$.

We choose to focus on the very positive features of our equation, its qualitative reasonableness and, especially, the presence of a threshold, rather than on the numerical errors in the position of the thresholds. The calculation of percolation thresholds, and nothing else, is itself a major problem,(1) while our theory yields a threshold along with the full exciton dynamics. Furthermore, as discussed, two and three dimensions provide a very severe test of any approximate treatment of fluctuations. Our theory should be better in three dimensions than in two; we suggest a good chance exists that the theory will be quantitatively accurate in three dimensions. Of course, many of the problems of experimental interest are three dimensional, although some are of lower dimension, e.g., if hopping is essentially confined to one crystal plane. Our next step, of course, will be to carry out the more computer time-consuming calculations in three dimensions.

We have studied the low $\langle\epsilon\rangle$ solution of our equation via the(5) scaling method, and it does not appear correct. Our theory was created as a high-density theory, and no stroke of luck has caused it to be valid at low density as well.

In conclusion we are eager to use the fledging theory to make new predictions and to interpret the next generation of time-resolved exciton migration experiments. If the theory does turn out to be quantitative in three dimensions on some test lattices, we simply can calculate $D_{\mathbf{k}}(z)$ for any indicated $T(\mathbf{r}_{ij})$ with an expectation of good results. If the finite lifetime of excitons must be treated, this can be done by addition of dissipative term to the master equation which does not complicate the ensuing analysis. Even where the theory does not give an exact $\langle\epsilon\rangle_c$ we can, as in much of the theory of critical phenomena, study the behavior of D near the threshold, i.e.,

$$D\left(\frac{\langle\epsilon\rangle - \langle\epsilon\rangle_c}{\langle\epsilon\rangle_c}\right)$$

An experimental study of such behavior would be very interesting.

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