Anomalous Diffusion in Amorphous Semiconductors

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1 Introduction

In 1975 Scher and Montroll [4] proposed a model of transport in a disordered medium (anomalous diffusion in an amorphous semiconductor) as a continuous-time random walk. This work has been quoted often, due to its applicability to other problems and because the experimental data agreed with the theoretical results amazingly well. They shined light onto a sample of amorphous semiconductor and measured the current coming out. There are two regimes in the amount of current exiting from a sample: near the exit side, and far from it. Far from the exit face, the movement of the electrons in the sample can be thought of as a continuous-time random walk in free space. A boundary must be imposed when the electrons get close enough to the edge. In order to calculate the two different scalings, Montroll and Scher developed a new mathematical theory [2] based on the idea of a continuous-time random walk. It is possible to get this scaling in an easier way, but Scher and Montroll's method is quite impressive and accurate, giving a constant term as well as the time dependence of the current.

Diffusion on a comb is another interesting model of continuous-time random walks. This model describes random waiting times as the length of time a walker is on a tine of a comb rather than moving in the desired direction. The probability density function for the length of time between steps is the length of time that it takes for the walker to return to the origin (intersection of the comb's tine and backbone) once it has deviated from the proper path.

2 Scher and Montroll's Work

Scher and Montroll performed an experiment in which they transmitted a pulse of light into a sample, creating electron-hole pairs. The imposed electric field caused the holes to migrate across the sample, creating a current $I(t) = evn$, where e is the amount of charge per electron, v is the average velocity of a hole, and n is the hole density at the exit face of the sample, $x = L$. The exit face of the sample is modeled as an absorbing surface, so that all holes that hit the surface join the current coming out of it. The apparatus for this experiment is shown in figure 1.

The expected current, using a naive model without accounting for diffusion, is shown in figure 2. Departures from this shape due to a variety of factors based on the material's properties and the nature of RC circuits can be modeled as diffusion. When simple diffusion

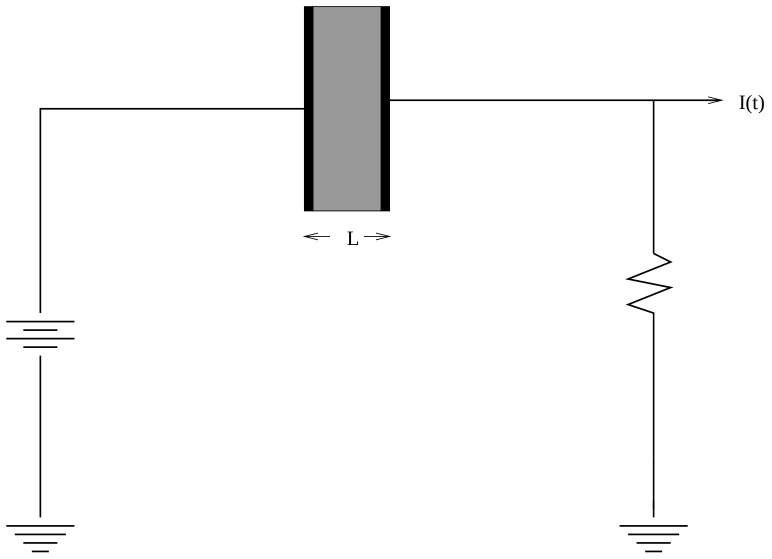

Figure 1: The experimental setup.

is taken into account, the current's plot becomes that shown in figure 3. However, in reality the current shown in figure 4 occurs, because anomalous diffusion takes place.

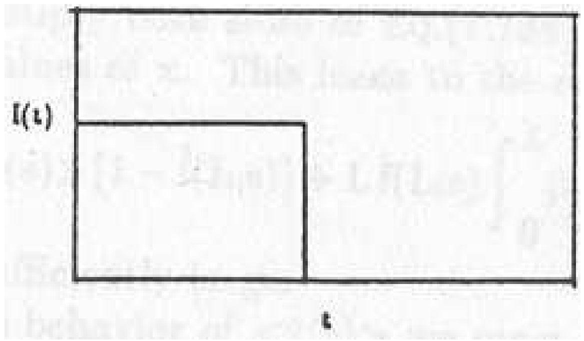

Figure 2: The expected appearance of $I(t)$, with no diffusion.

Scher and Montroll created a theoretical model of this diffusion that is remarkably accurate. They started by looking at traditional transport theory, where a series of Gaussian packets move in a way described by a Markoffian transport equation. However, this model did not account for all the data, so they changed tactics. They used a continuous-time random walk model of the holes in the sample created by the light pulse walking across the sample to the absorbing boundary. In this problem there are two regimes: diffusion of the hole when it is far from the absorbing boundary, and diffusion of the hole when it is near the absorbing boundary. The movement of the hole near the absorbing boundary is the movement of the hole far from it, but with an additional factor to account for the absorption. Scher and Montroll started with the "hopping-time distribution function" $\psi(t)$, and used $\psi(t)dt$ as the probability that a hole will move to the next cell within dt of arriving in its

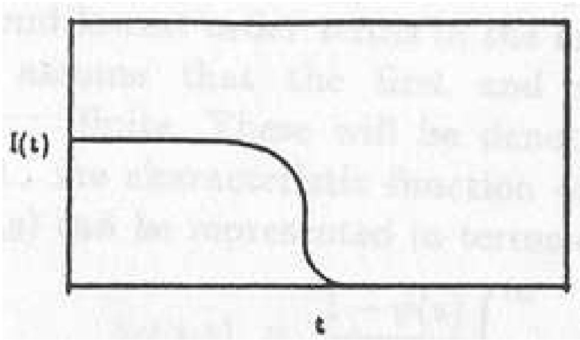

Figure 3: The appearance of $I(t)$ with diffusion.

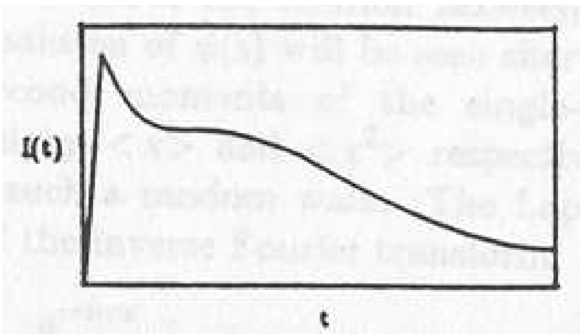

Figure 4: The appearance of $I(t)$ in truth, with anomalous diffusion.

cell. In a previous paper [2], Montroll and Scher developed a description of an asymmetric non-Markoffian continuous-time random walk near absorbing barriers. They used this information in their model for this phenomenon. They started with

$$I(t) = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} e^{s\tau}\hat{I}(s)d\tau\tilde{I}(s) \sim (1-\tilde{\psi}(s))(\sum xG(x-x_0,\tilde{\psi}) - (\frac{G(L-x_0,\tilde{\psi})}{G(0,\tilde{\psi})\sum xG(x,\tilde{\psi})}) \quad (1)$$

as a representation of the probability distribution function in terms of the Laplace transform of an equation they derived in their previous paper [2]. Here the ratio of the Gs is the Laplace transform of the function describing the time it takes for a hole to cross the lattice, $< F(L-x_0,\tau) >$.

Then Scher and Montroll used some equations that they derived in the second of their four appendices:

$$\frac{G(L-x_0,\tilde{\psi}(s))}{G(0,\tilde{\psi}(s))} \sim \alpha_1^{L-x_0} + (1-\alpha_1^L)\alpha_2^{-x_0}\alpha_1 \sim e^{-\epsilon}\alpha_2 \sim \kappa e^{\epsilon}\epsilon = \frac{1-\tilde{\psi}(s)}{< x >} \sim \frac{2s^{\frac{1}{2}}}{< x >} \quad (2)$$

They found that

$$< I(s) > \sim \frac{e^{(L-x_0)\epsilon}}{\epsilon}.$$

Plugging this last equation back into equation 1 and integrating in the complex plane by moving the contour so that it goes around the branch point of $< I(s) >$. Taking the two limits $(L-x_0)\epsilon$ much less than and much greater than one give the two desired behaviors:

$$I(t) \sim \frac{< x >}{c\Gamma(\alpha)\tau^{1-\alpha}}, (L-x_0)\epsilon >> 1 \quad (3)$$

$$I(t) \sim \frac{1}{2} < x > (\frac{L-x_0}{< x >})^2 \frac{c}{-\Gamma(-\alpha)\tau^{1+\alpha}}, (L-x_0)\epsilon << 1 \quad (4)$$

So the two exponents of τ, $-1+\alpha$ and $-1-\alpha$, add to -2, so α is irrelevant.

Here is another, simpler, but not as interesting or accurate, derivation of the scaling near the boundary. It assumes that the problem has been solved far from the boundary. This derivation is from Weiss [5], pages 303-309. It uses the same concepts as Scher and Montroll's version, but is easier to understand while still giving the desired scaling. Suppose the light shined on the sample at $t = 0$. Then the mean hole position at time t is $< x(t) >$ and the velocity $v(t) = \frac{d< x(t) >}{dt}$. The electric field produces a net motion of holes towards $x = L$, which acts like a bias in the transition probability. This can be described as

$$< x(t) > \sim < x > (\frac{t}{T})^{\alpha}$$

where T is the time between steps and α is between zero and one. Then $v(t) \sim t^{\alpha-1}$ asymptotically. Now assume that L is big enough that the hole movement is not influenced by the absorbing boundary at $x = L$ until after the average distance $< x > \sim < x(t) >$. From now on a variable with a tilde on top of it will represent the Laplace transform of that quantity.

Weiss only used this to model the behavior of holes near the exit point. Let $P(x,t)$ be the probability density function of holes at time t near the boundary. $P_0(x,t)$ is the same as P, but with no boundary present. $f(L,t)$ is the time it takes a hole to reach L. First, a relationship between these quantities must be specified.

$$P(x,t) = P_0(x,t) - \int_0^t f(L,\tau)P_0(x-L,t-\tau)d\tau$$

seems to work well. This says that the probability density function near the boundary is the probability density function that would exist without the boundary, but with an additional part which comes from the boundary's presence. Taking the Laplace transform gives

$$\tilde{P}(s,x) = \tilde{P}_0(x,s) - \tilde{f}(L,s)\tilde{P}_0(x-L,s).$$

Using the relation

$$P_0(L,t) = \int_0^t f(L,\tau)p_0(0,t-\tau)d\tau$$

and solving for f gives

$$\tilde{f}(L,s) = \frac{\tilde{P}_0(L,s)}{\tilde{P}_0(0,s)}.$$

Then this can be substituted back into the original equation, giving

$$\tilde{P}(x,s) = \tilde{P}_0(x,s) - \frac{\tilde{P}_0(L,s)}{\tilde{P}_0(0,s)}\tilde{P}_0(x-L,s). \tag{5}$$

This is the desired relationship between the probability density function with the boundary and the probability density function without the boundary.

The next step is to find $<\tilde{x}(s)>$. The average displacement of the random walk in free space is $<x_0(s)>$. Multiplying both sides of equation 5 by x and integrating over all values of x gives

$$<\tilde{x}(s)>=<x_0(s)>(1-\tilde{f}(L,s)) + L\tilde{f}(L,s)\int_0^L \tilde{P}_0(x,s)dx$$

when L is large enough. When s is small, it is acceptable to make the approximation

$$\tilde{\psi}(s) \sim 1 - (sT_0)^\alpha + (sT_1)^\beta$$

where β is greater than or equal to twice α. Then

$$\tilde{P}_0(x,s) = \frac{1-\tilde{\psi}(s)}{2\pi s}\int_{-\infty}^{\infty} \frac{e^{-i\omega x}}{1-\tilde{\psi}(s)C(\omega)}d\omega$$

where $C(\omega)$ is the characteristic function of the random walk. This assumes that the first and second moments of the displacements are finite. Then expand C and $\tilde{\psi}$ around $\omega = s = 0$ and integrate the result:

$$\tilde{P}_0(x,s) = \frac{1-\tilde{\psi}(s)}{2\pi s}\int_{-\infty}^{\infty} \frac{e^{-i\omega x}}{1-\tilde{\psi}(s)(1_i<x>\omega - \frac{<x^2>}{2}\omega^2}d\omega \tag{6}$$

This equation is much easier to integrate by rewriting part of the integral as

$$\frac{1}{1-\tilde{\psi}(s)(1+i<x>\omega-\frac{<x^2>}{2}\omega)}=\int_0^\infty e^{-1-\tilde{\psi}(s)(1+i<x>\omega-\frac{<x^2>}{2}\omega)}.$$

Using this shows that

$$\tilde{P}_0(x,s)=e^{\frac{<x>x}{<x^2>}(1-\sqrt{1+\frac{2<x^2>(1-\tilde{\psi}(s))}{<x>^2\tilde{\psi}(s)}})}.$$

As s goes to zero, $1-\tilde{\psi}(s)$ goes to $(sT_0)^\alpha$. Then $\tilde{f}(L,s)\sim 1-as^\alpha-bs^{2\alpha}$.

Doing another approximation for small s gives

$$<\tilde{x}_0(s)>=\frac{<x>}{s(1-\tilde{\psi}(s))}\sim\frac{<x>}{T^\alpha s^{\alpha+1}}$$

which is the same as saying

$$<\tilde{x}_0(s)>\sim\frac{<x>}{T^\alpha}(\frac{a}{s}+\frac{b}{s^{1-\alpha}}+L\int_0^L\tilde{P}_0(x,s)dx$$

where the integral term becomes $L^2s^{\alpha-1}$. Then since $<\tilde{v}(s)>=s<\tilde{x}(s)>$, $<v(t)>\sim kt^{-(1+\alpha)}$ near the border.

Both Scher and Montroll and Weiss have found the same scaling laws for this case of anomalous diffusion. Several other papers have been written with data from the sort of experiment they describe. The agreement between this data and the theory is amazing. Scher and Montroll and Weiss have taken data from some of these other papers and put it into their own to show the agreement. This data is shown in figures 5 and 6.

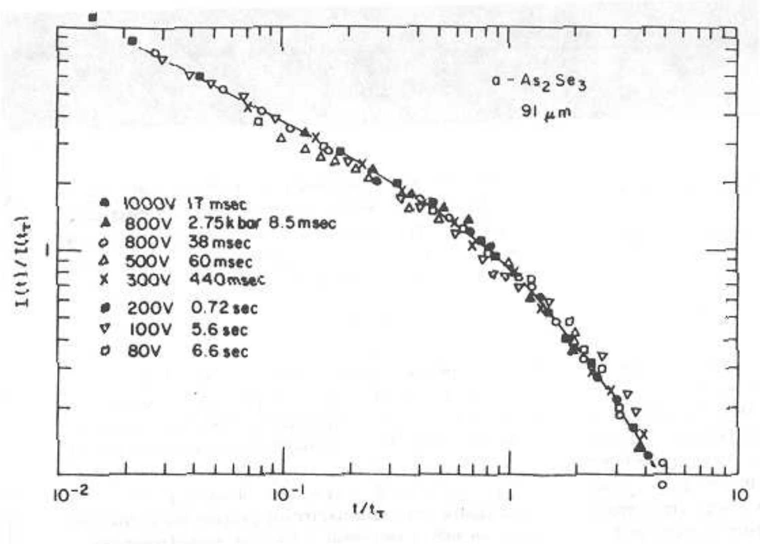

Figure 5: Some data from Scher and Montroll's paper. This data shows that there is a change in scaling.

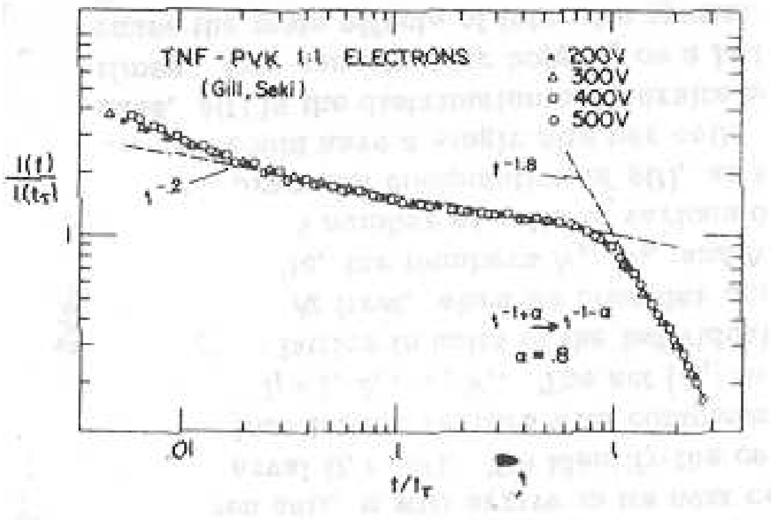

Figure 6: More data from Scher and Montroll's paper. The change in scaling is more clearly demonstrated here, and the sum of the exponents is clearly -2.

Scher and Montroll [4] think that their work shows the limits of previous theories of mobilities and accounts for the change in current that is always observed. In the future they would like to see this kind of model used for other scenarios. The next step in this research would be to calculate the transition rate of various materials to find out where the critical point is, and find a value for α.

3 Diffusion on a Comb Structure

Weiss suggests that examining percolation clusters can provide insight into transport in a disordered medium, the problem that Scher and Montroll attacked. The comb model is the simplest model for a percolation cluster. It was originally designed to examine transport on a fractal medium because it can be made as complex as necessary but still retains a simplicity that makes modeling it easy. In this idealized model there are no loops formed by tines connecting to one another, and the tines are evenly spaced along a backbone.

Diffusion on a comb or comb-like structure can be analyzed as a continuous-time random walk with a wide range of waiting times [1]. A particle moves along the x-axis of the comb depicted in figure 7, but it can get caught in the tines of the comb as it goes along. Getting caught in the tines contributes to the wide range of waiting times. When the walker takes a step in the y direction - in one of the tines - it does not count because the only steps that are considered useful are those along the x-axis.

Then the probability distribution for waiting times $\psi(\tau)$ decays like $\tau^{-3=over2}$. This is because the waiting time between steps along the x-axis is equivalent to the time it takes for the walker to return to 0 after it has gone off on one of the tines. This scaling assumes that L is very large, producing anomalous diffusion along the x-axis.

If L is finite, the time the walker spends in a tine $\tau_c \sim \frac{L^2}{D_0}$, where D_0 is the diffusion

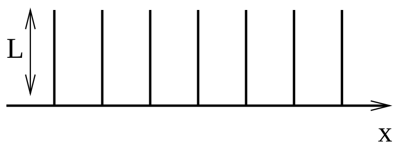

Figure 7: A comb structure for demonstrating anomalous diffusion.

coefficient for the tine. If τ is much greater than τ_c, the average time the walker spends exploring a tine, $<\tau>$, becomes

$$<\tau>\sim \int_0^{\tau_c} \frac{1}{\sqrt{\tau}} d\tau \sim L.$$

Then normal diffusion returns, but the diffusion constant depends on the length of the tines ($D \sim \frac{1}{L}$).

In a row of convection rolls, a particle in one convection roll travels along the flow lines, but also diffuses [1]. The convection rolls are shown in figure 8. Because of diffusion the particle can jump from one convection roll to another. Each roll traps the particle for some length of time, like the tines of the comb in the previous example delayed the walker. The probability distribution of the time between steps is $\psi(\tau) \sim \tau^{-(1+\alpha)}$ when τ is less than or equal to $\frac{L^2}{D_0}$, where L is the diameter of the convection roll. This is like the scaling in the previous section, but it is also like the scaling for Scher-Montroll diffusion.

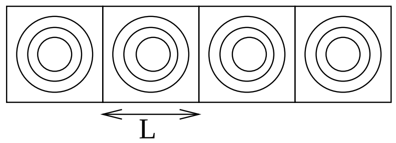

Figure 8: Diagram of an array of convection rolls.

In this system the walker moves along an array of cells that are sticky - they drag the walker down for some length of time. The length of time is random and may be very long or very short. Within a convection roll, it is convenient to think of the flow lines as a set of sites (i), numbered from 1 (the closest to the edge of the roll) to i. Then the particle does a random walk along the lattice made up of flow lines. So the probability of leaving the roll is the probability of returning to the origin, in this case the site that the walker entered the roll at. The time spent in the roll is dependent upon the flow patterns, especially the time it takes for a bit of fluid to go all the way around one of the flow lines.

4 Conclusion

Keeping some kind of structure in space is useful for a model based on a random walk because often there is some sort of structure in reality. In Scher and Montroll's semiconductors, the lattice is the formation that the atoms of the semiconducting material have arranged themselves in. Using a characteristic function helps to find an exact solution for the random walk and generate moments [5]. Scher and Montroll used these things to their advantage and found an exact solution to a problem that had been troubling researchers for some time.

These two models of anomalous diffusion show that continuous time random walks are related to the real world. Scher and Montroll's work provides an excellent model for a process that researchers had trouble understanding for a long time. They, along with others, spent nearly ten years developing the math for their theory of transport, starting with a 1965 paper by Montroll and Weiss [3] that created one form of continuous-time random walk. In order to understand it completely, it would be necessary to go through all 10 years it. It is a good theory but has a lot of background work necessary to understand it completely. It would also be interesting to look at the same problem using a comb type of model. This may give some interesting results and perhaps a model that is not as convoluted as Scher and Montroll's.

References

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