CONTINUOUS-TIME RANDOM-WALK IN DISORDERED SYSTEMS

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Introduction

Diffusion of excitations in a medium of irregular potential has remained a difficult problem. Free transport is the biggest casualty caused in going from an ordered solid to a disordered solid. Environment at different points in a disordered medium is different, consequently a carrier feels different potential as it moves around and experiences scattering due to the fluctuating potential. In situations where the acattering is strong and occurs in random directions, the carrier may get localized [1] in space in presence of an external d.c. field. Such a carrier does not contribute to the electrical conductivity and has a wave function which is peaked around a centre in contrast to the uniformly spread Bloch wave function.

For a carrier of given energy the medium can be divided into 'closed' regions of various spatial extents which can offer enough fluctuations to localize the carrier, as well as 'open' regions through which the carrier can move across and contribute to the conductivity. A trapped carrier can be made to 'hop' to the neighbouring regions by giving it thermally the required activation energy. Thus the transport at non-zero temperature in a disordered medium is to be viewed as hopping along traps and open conducting regions with the traps playing the role of 'immobilizers'. The carrier spends some time in a trap before transition occurs to a neighbouring region, the length of time being decided by the amount of fluctuation offered by the trap. Thus there is a distribution of lengths of time the carrier spends in the traps.

Montroll and coworkers [2,3,4] gave the continuous-time random-walk (CTRW) model to study the above hopping assisted diffusion process. The model assumes a configurationally averaged medium after imbedding all informations of disorder into the distribution function of 'waiting times' (spent in traps), $W(t)$. The carrier, executing random walks in a periodic medium, can abruptly change its position to number of others, each choice weighted by a value of $W(t)$.

It is quite clear that in the CTRW model averaging must have destroyed lot of new and crucial informations expected entirely from the disordered nature of the medium. Experiments [4] have revealed that the transport in disordered solids has a very distinct 'dispersive' characteristic, conceptual visualization of which is not possible in an averaged medium where due to the absence of traps one cannot distinguish 'trapping' from diffusion. Another problem arises when one tries to understand the frequency dependent response to a.c. field of the systems exhibiting dispersive transport [5]. For other criticisms of CTRW model see Schmidlin [6], Ngai and Liu [7] Chekunaeu et al [8] and Rudenko and Ankhipov [9]. All the criticisms emphasize the fact that localized and conducting states should not be treated on equal footing.

So the CTRW model should be generalized to treat the quantum states in the system to be inequivalent. We shall do this in the following [10].

The Generalized CTRW Model

Consider the probability to just arrive at site n in time interval $(t,t+\Delta t)$ in N steps, $R_N(n,t)\Delta t$, which satisfies the recursion formula,

$$R_{N+1}(n,t) = \int_0^t d\tau \sum_{m\neq n} \psi_{nm}(t-\tau)R_N(m,\tau) \tag{1}$$

where $\psi_{nm}(t)$ is the probability per unit time that transition from a state situated at m occurs to a state situated at n in time t. The states situated at n and m are equivalent in an averaged medium, so ψ_{nm} depends only on the separation between n and m. However, in disordered medium the states at n and m shall be different in nature, so this information should also be included in the transition probability. Random walk shall now be represented by the following equation,

$$R_{N+1}(n_\alpha,t) = \int_0^t d\tau \sum_{m_{\alpha'}\neq n_\alpha} W_{n_\alpha m_{\alpha'}}(t-\tau)\; R_N(m_{\alpha'},\tau), \tag{2}$$

where α and α' represent the nature of states at n and m. Following conditions are satisfied by ψ_{nm} and $W_{n_\alpha m_{\alpha'}}$:

$$\sum_n \psi_{nm}(t) = 0 \; ; \; \sum_{n_\alpha} W_{n_\alpha m_{\alpha'}}(t) = 0, \tag{3a}$$

and

$$\int_0^\infty \sum_{n\neq m} \psi_{nm}(\tau)d\tau = 1 \; ; \quad \int_0^\infty \sum_{n_\alpha\neq m_{\alpha'}} W_{n_\alpha m_{\alpha'}}(\tau)d\tau < 1. \tag{3b}$$

Condition (3a) is essential for conservation of probability as will be seen later. Condition (3b) is of central importance — in the case of ψ (i.e. averaged medium) it says that the carrier must leave the site m eventually, while in the case of W (i.e. unaveraged medium) the carrier may not leave the site m even if infinite time has elapsed. Some more insight into the difference between the averaged and unaveraged mediums is achieved if we decouple ψ and W in space and time parts as,

$$\psi_{nm}(t) = \vartheta_{nm}k(t), \tag{4a}$$

and

$$W_{n_\alpha m_{\alpha'}}(t) = V_{n_\alpha m_{\alpha'}} k_{m_{\alpha'}}(t), \tag{4b}$$

where ϑ and V cause the transition from m to n and k takes care of the fact that this transition occurs after time t; note the dependence of k on the nature of state at m in the unaveraged medium. For ϑ and V we have the following conditions,

$$\sum_{n} \vartheta_{nm} = 1 \quad \text{with} \quad \vartheta_{mm} = 0 \; ; \tag{5a}$$

and

$$\sum_{n_\alpha} V_{n_\alpha m_{\alpha'}} = 1 \text{ with } V_{m_\alpha, m_{\alpha'}} > 0 \; . \tag{5b}$$

Also note that, $\vartheta_{mm}(t) = 0$ (6a)

while $W_{m_\alpha, m_{\alpha'}}(t) = -(1-V_{m_\alpha, m_{\alpha'}})k_{m_{\alpha'}}(t)$. (6b)

Thus,

$$\int_0^\infty \sum_{n_\alpha \neq m_{\alpha'}} W_{n_\alpha m_{\alpha'}}(\tau)d\tau = \underbrace{(1-V_{m_\alpha, m_{\alpha'}})}_{\uparrow} \underbrace{\int_0^\infty k_{m_{\alpha'}}(\tau)d\tau}_{\uparrow} \tag{7}$$

= 0   = 1   : for averaged medium

$>$ 0 $<$ 1   : for unaveraged medium

Now we come back to (2) and eliminate the step variable N by summing over all paths of number of steps varying from 0 to ∞ ; using the initial condition that the carrier was at the initial state '0' at time t = 0, we obtain,

$$R(n_\alpha,t) - \int_0^t d\tau \sum_{m_{\alpha'} \neq n_\alpha} W_{n_\alpha m_{\alpha'}}(t-\tau) \, R(m_{\alpha'},\tau) = \delta_{n_\alpha o} \, \delta(t-0) \; . \tag{8}$$

Having considered the probability to just arrive at a given state at a given time we turn to our main object of answering the following question. Suppose the carrier, which was at state '0' at t = 0, reaches the state n_α at time τ , then what is the probability that it can be found at n_α at a later time t? One asks this question because a random walker starting from an arbitrary origin can choose from a large variety of paths to arrive at n_α at different times. We can alternatively put it as follows. A carrier having arrived at n_α at time τ ($<$t) remains unmoved in the remaining time (t-τ). This is easily expressed as follows,

$$P(n_\alpha,t) \equiv P(n_\alpha,t|0,0) = \int_0^t d\tau \; \phi_{n_\alpha}(t-\tau)R(n_\alpha,\tau), \tag{9}$$

where $P(n_\alpha,t)$ is the conditional probability that the carrier initially at '0' is found at n_α at time t, and $\phi_{n_\alpha}(t-\tau)$ is the probability for remaining unmoved for time (t-τ). It is important to note that in a random medium the carrier may remain unmoved while at n_α also because n_α may be a trap. The subscript n_α indicates this dependence of ϕ on the nature of state at n. Total probability to remain unmoved in interval (0,t) at n_α is,

$$\phi_{n_\alpha}(t) = 1- \int_0^t d\tau \sum_{g_{\alpha'} \neq n_\alpha} W_{g_{\alpha'}, n_\alpha}(\tau) \; . \tag{10}$$

Eliminating R from (9) we obtain,

$$P(n_\alpha, t) = \phi_{n_\alpha}(t)\,\delta_{n_\alpha o} + \int_o^t d\tau \sum_{m_{\alpha'} \neq n_\alpha} W_{n_\alpha m_{\alpha'}}(t-\tau) P(m_{\alpha'}, \tau). \qquad (11)$$

This is the generalized CTRW equation. Probability is conserved due to (3a). As discussed earlier $W_{n_\alpha m_{\alpha'}}$ is not a simple function of separation between the positions of the states, although it can be simplified and made function only of separation between positions of states by averaging over the positions of the states (note that this is different from configurational averaging and $V_{m_\alpha, m_{\alpha'}}$ remains non-zero).

We can rearrange (11) and cast it in the form of a rate equation in probability. It is convenient to first take the Laplace transform of (11),

$$\tilde{P}(n_\alpha, z) = \tilde{\phi}_{n_\alpha}(z)\,\delta_{n_\alpha o} + \sum_{m_{\alpha'} \neq n_\alpha} \tilde{W}_{n_\alpha m_{\alpha'}}(z)\,\tilde{P}(m_{\alpha'}, z), \qquad (12)$$

and then rearrange it to write,

$$z\,\tilde{P}(n_\alpha, z) - \delta_{n_\alpha o} = \sum_{m_{\alpha'}} \tilde{M}_{n_\alpha m_{\alpha'}}(z)\,\tilde{P}(m_{\alpha'}, z), \qquad (13)$$

where, $$\tilde{M}_{n_\alpha m_{\alpha'}}(z) \equiv \left[(1-\delta_{n_\alpha m_{\alpha'}})\,\tilde{W}_{n_\alpha m_{\alpha'}}(z) - \delta_{n_\alpha m_{\alpha'}} \sum_{g_{\alpha'} \neq n_\alpha} \tilde{W}_{g_{\alpha'}, n_\alpha}(z)\right] / \tilde{\phi}_{n_\alpha}(z). \qquad (14)$$

Now taking the Laplace inverse-transform of (13), we get,

$$\dot{P}(n_\alpha, t) = \sum_{m_{\alpha'}} \int_o^t d\tau\; M_{n_\alpha m_{\alpha'}}(t-\tau) P(m_{\alpha'}, \tau). \qquad (15)$$

This is the familiar generalized master equation. Thus we learn that the GCTRW equation is an exact transport equation and describes a non-Markovian stochastic process [10].

Localization and Dispersive Transport

The transport equation (15) can be useful for understanding certain problems in localization [11] and the problems related with the dispersive nature of transport in disordered systems which, as pointed out in the beginning, can not be explained in the averaged medium - CTRW framework.

As already stated localization is of central importance in disordered solids and is responsible for lots of peculiar physical properties observed in such systems. We will describe the existing localization picture very briefly and then discuss a finer modification introduced in it due to considerations based on (15). Thereafter we will come to dispersive transport which is a consequence of localization and is intimately related with the said modification in the localization picture.

The picture that has emerged from theoretical analyses and is supported by experiments also is the following. In the energy spectrum the energies near the band centre correspond to conducting states and those towards the band edges correspond to trap (or localized) states; the two kinds of states are separated sharply at energies called 'mobility edges', E_c. Localization is defined in terms of a 'stay-put' probability which is same as our $P(n_\alpha,t)$ with n_α as the origin:

$$\lim_{t\to\infty} P(n_\alpha,t) \begin{cases} = 0 & \Rightarrow \text{conducting states} \\ > 0 & \Rightarrow \text{localized states .} \end{cases} \tag{16}$$

There are conflicting views about the nature of transition from localized regime to conduction regime. According to one point of view put forward by Mott and coworkers [12], as the mobility edge is approached, conductivity becomes smaller and smaller and takes a minimum value, the 'minimum metallic conductivity', before abruptly becoming zero. The other point of view due to Cohen [13] favours a continuous transition, i.e. the conductivity goes to zero in a continuous manner. This problem can be studied in terms of rate of diffusion, i.e. how $P(n_\alpha,t)$ approaches zero in the vicinity of E_c since $P(n_\alpha,t)$ is related with mobility [3]. For this purpose we introduce the following integral,

$$\mathcal{J} = \int_0^\infty P(n_\alpha,t)\,dt, \tag{17}$$

which enables us to distinguish between rates of diffusion as follows,

$\lim_{t\to\infty} P(n_\alpha,t)$	$\mathcal{J}$		
$= 0$	$< \infty$	$\Rightarrow$	fast diffusion
$= 0$	$= \infty$	$\Rightarrow$	slow diffusion
> 0	$= \infty$	$\Rightarrow$	no diffusion

The regions of fast and no diffusion are well established. If the existence of the new intermediate regime of 'slow diffusion' could be established, then we could conclude that the conductivity goes to zero in localized regime gradually and there is no minimum metallic conductivity. This, indeed, is possible to show [11] with the help of the rate equation (15). All one has to do is to construct the kernel M which is possible if the waiting-time distribution W can be known. Since our aim is to investigate the vicinity of E_c on conduction side in terms of the divergence of the integral, $\mathcal{J}$, given that the stay-put probability vanishes in the limit $t\to\infty$, we can suitably choose forms for W in conduction and localized regimes so as to satisfy (16) and match them at the E_c. For the matching we make use of experimental results on photoconduction [3,4]. The ansatz for W and the calculational details are discussed in [11].

Now we come to the dispersive nature of transport in presence of localized states. The photoconductivity experiments performed on many semiconducting systems show that a bunch of photo-excited electrons which can be viewed as a Gaussian packet gets deformed and broadened as it moves under an electric field. If the disorder is moderately large the packet disperses into a very wide distribution of carriers with the probability of finding some of the carriers near the starting point remaining considerable even after a large time. The reason is simple. Imagine a packet of carriers starting from an electrode and moving towards the other. On the way they come across traps where they can stop for different durations depending upon the holding strengths of the traps. While some of them remain unmoved, others move ahead. In this manner the packet becomes broader and broader as time elapses.

The nature of transport is not highly dispersive in all regimes. The ansatz for W given in [11] in the GCTRW framework reveals the following picture. In the small disorder-metallic regime transport occurs in the form of mildly broadened Gaussian packet. In the moderately high disorder-slow diffusion regime near E_c, transport occurs in highly dispersive non-Gaussian manner. In high disorder insulating regime the carriers move about among traps in the form of a broadened Gaussian packet. Thus the non-Gaussian transport is an attribute of the new intermediate regime of slow diffusion [14].

An interesting account of thermal equilibrium between mobile and localized carrier fractions in a system with traps having arbitrary energy distribution is given in a series of papers by Rudenko and Arkhipov [9]. They have found that the state of non-equilibrium persists for rather a long time, however, when the equilibrium is attained the carriers form a Gaussian packet which moves with a constant velocity. The dispersion of the packet grows with time as $t^{1/2}$ and the ratio between the dispersion and the displacement of the packet mean decreases with time as $t^{-1/2}$.

Finally we will make a comment on the observed frequency dependent response to a.c. field. To explain this, it is not sufficient to consider the quantum states to be inequivalent and simple traps scattered here and there in the system, instead one must also include the possibility of complex traps or clusters of closely lying traps. In the former situation, when the carrier is free, it drifts in phase with the field and when it occassionally stops in a trap it does not contribute to the current at all, while in the latter situation an occupied complex trap acts as a 'relaxation dipole' — the carrier can oscillate with the a.c. field but out of phase by an amount given by the relaxation time of the dipole. It is thus clear that besides configurational averaging it is also essential that no assumptions should be made regarding the number and arrangement of traps (unlike the work by Scher and Wu [15] who assume a periodic distribution of traps).

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