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THE THEORY OF TRANSPORT IN AMORPHOUS SEMICONDUCTORS

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Abstract.- The theory of transport in disordered systems is approached using the Master equation point of view. Emphasis is laid on a microscopic interpretation. An approximate selfconsistent theory is presented with which it is possible to evaluate hopping d.c. and a.c. conductivity and Hall mobility. The theory is compared with computer simulations and experiments on amorphous semiconductors. The method is extended to treat diffusion limited relaxation and recombination and applied to evaluate the spin-lattice relaxation time of electronic and nuclear spins in amorphous semiconductors.

Introduction.- Electronic hopping transport, nuclear and electronic spin diffusion and relaxation, recombination and trapping in the region of localized states in amorphous systems are all examples of phase incoherent diffusion problems. The particle or excitation density \( n_i(t) \) generally obeys a Master equation involving diffusion and relaxation terms in a disordered network of localized states

\[
\frac{dn_i(t)}{dt} = -\sum_j W_{ij} n_i(t)(1-n_j(t)) + \sum_j W_{ji} n_j(t)(1-n_i(t)) - \delta \frac{n_i(t)}{n_0(t)} \tag{1}
\]

where the \( W_{ij} \) represent transition frequencies from a site "i" to a site "j", and the loss rates \( \delta \) in general will differ from site to site. Depending on the problem under consideration, the \( \delta \) can for example represent spin relaxation or recombination rates. In the absence of loss terms this equation describes ordinary diffusion in a disordered system. This type of description has wide range of applications. Here I want to concentrate on three particularly interesting applications in the field of amorphous semiconductors.

In the first place there is the hopping conductivity problem. In a large class of evaporated and sputtered materials one experimentally finds a frequency dependent hopping conductivity\(^1\) of the form

\[
\text{Re} \sigma_{xx}(\omega) = \sigma_{xx}(0) + \sigma_{xx}^S \omega^s, \ 0 < s < 1
\]

where \( \sigma_{xx}(0) \) is the d.c. contribution which usually obeys the Mott law

\[
\sigma_{xx}(0) = \sigma_0 \exp \left( \frac{-1}{T_0/T} \right)^{1/4}
\]

The exponent \( s \) is a function of temperature with \( s = a - bT \). A typical and particularly complete set of data taken by Balkan and Long\(^2\) on a-Ge are shown in fig. (1).

In the Miller-Abrahams\(^3\) type of approach one transforms the microscopic diffusion problem illustrated by (1) into a macroscopic conductance network. The d.c. conductivity is evaluated using percolation techniques\(^4,5\) and yields in 3 dimensions...
for a constant density of states
the Mott law with $T_0 = 2.7 T_0(Mott)$. The
frequency dependence however, is usually
attributed to pair processes with
electrons hopping forward and backward
between sites producing fluctuating
electric dipole moments with a distribu-
tion of relaxation times. The Austin-
Mott $^6$, Pollak-GBuralle $^7$ pair theories do
indeed yield an $\omega^s$ law, the exponent $s$
is however not dependent on temperature
as found experimentally. To remedy this
discrepancy in the framework of the
pair model $^{11,12}$, for example has
used the barrier model of $^{39}$ in
place of the usual phonon assisted hop-
ning rates. We shall see that this
difficulty is simply due to the artificial
separation between a.c and d.c
influence.

In fact the macroscopic network inter-
pretation, though extremely useful for
accurate computation of the d.c
conductivity, has obscured somewhat the
physics and the generality inherent in the
microscopic approach.

A second example is the spin re-
xaction in a-Si and a-Ge. Ex-
erimentally Connell and Pawlik $^{11}$,
and Vogel-Grote and Stuke $^{10}$ observe
that the temperature dependent line-
width can be written as

$$\Delta H_{pp}(T) = \Delta H_{pp}(0) + C (\sigma_{xx}(0))^\mu,$$

where $0.5 < \mu < 1$ (fig. 2).

The temperature dependent linewidth is therefore proportional to the d.c
conductivity to the power of an ex-
ponent $\mu$ which is usually less than
1 (fig. 2). Since $\Delta H_{pp}(T) - \Delta H_{pp}(0)$
is caused by lifetime broadening or
spin lattice relaxation, the depend-
ence on $\sigma_{xx}$ is a clear indication
that hopping is the basic mechanism
responsible for the relaxation pro-
cess $^{12}$, transporting the spin to
particular fast relaxing centres and
bonds. A microscopic random walk
point of view is inescapable in this
case.

A third example is spin-latt-
cice relaxation of Hydrogen nuclear
spins in a-Si:H. The data of Carlos
and Taylor $^{13}$ are shown in fig. (3).
These authors proposed a model in
which the spin excitation diffuses via
dipolar spin-diffusion to par-
ticular relaxing centres: hydrogen
clusters coupled to structural re-
xalation modes. By deuterising the
samples, Reimer et al. $^{14}$ have recent-
ly supplied direct experimental
The motivation of the present work is therefore to present a microscopic theory of diffuse transport capable of reproducing the well established percolation results in the d.c limit but valid for all densities, frequencies, and temperatures. The theory is then generalized to include random relaxation or recombination processes and applied to ESR and NMR. The realization that a microscopic random walk theory of transport is more powerful and more general is not new. This has been the object of the Continuous Time Random Walk CTRW description due to Montroll, Scher and Lax. In the CTRW formalism, one maps the true random walk onto a regular lattice and assumes that all the disorder can be included in a single site waiting time distribution function $\psi(t)$. This assumption has now been given rigorous justification by Klafter and Silbey. The approximation for $\psi(t)$ used by Scher and Lax however yield a d.c. conductivity which is the Miller-Abrahams value rather than the correct percolation result. As far as we know, the theory has not been generalized to treat asymmetric hopping frequencies characterising for example hopping in amorphous semiconductors.

The conductivity. - Let us begin by considering the conductivity. Several authors have shown how to linearise the Master equation in the presence of an electric and a magnetic field. The general expressions for the frequency dependent longitudinal ($\sigma_{xx}(i\omega)$) and transverse ($\sigma_{xy}(i\omega)$) (Hall) conductivity can be written respectively, where $e$ is the electronic charge, $V$ is the volume, $x_i$ ($y_i$) are the $x$ ($y$) coordinates of the "i" th site, $x_{ij} = (x_i - x_j)^2$, the pointed bracket denotes a configurational average, and $F_i = f_i(1 - f_i)$ where $f_i$ is the Fermi function in the limit of infinite Hubbard repulsion energy. The quantity $G_{i,j}(i\omega)$ can be interpreted as a Green function or matrix element of the operator $(i\omega - H)^{-1}$, where $\chi$ is analogous to a tight binding Hamiltonian with diagonal element $\chi_{i,i}(H) = -\frac{1}{\epsilon_i} - \frac{1}{\epsilon_i}$ and off-diagonal terms $\chi_{ij}(H)$ are magnetic fields. $\Delta G_{i,j}(H)(i\omega)$ is the linear term in an expansion of $G_{i,j}(H)(i\omega)$ in powers of $H$. The $G_{i,j}(H)(i\omega)$ represents the Fourier-Laplace transform of the time dependent Green function $G_{i,j}(H)(t)$ which is the solution of the linearized Master equation,

$$\frac{dn_{i,j}(t)}{dt} = - \sum_j n_{j,i}(t) \chi_{i,j}(H) + \sum_j \chi_{i,j}(H) n_{j,i}(t)$$

and can be given a microscopic interpretation as describing the probability of finding the particle at site "j" at time $t$ if it was created at site "i" at time $t=0$. The conductivity of Hydrogen in a-Si:H as a function of temperature; $\nu_0$ is the resonance frequency. From ref. (13)
The problem that one faces in evaluating $\sigma_{y_0}(x)$ is twofold. For arbitrary disordered networks an exact solution is not possible so that one must 1) find a reasonable approximation to the probability function $G_{ij}(t)$, in other words to the sum over all paths a particle can take in going from "i" to "j", 2) carry out the configurational average over space and energy. To deal with the path summation we expand $G_{ij}(i\omega) = \langle i | (i\omega - k)^{-1} | j \rangle$ using the renormalized perturbation expansion (RPE) \textsuperscript{21}. This has the great advantage of eliminating all the repeated indices leaving only self-avoiding walks from "i" to "j". The basis of our approximation which is discussed in detail in ref. (21,22) is now to develop systematic two-site, three-site etc. selfconsistent approximations. In the two-site theory, we treat pair memory effects exactly and approximate the 3-site and higher order memory effects (i.e. closed loops). Similarly in the 3-site theory we keep up to three site memories and approximate higher order effects. This means that the "particle" always remembers the previous or the previous two sites it has visited on its paths and randomises over the rest. Selfconsistency is achieved by using in each case the corresponding Effective Medium Approximation (EMA) \textsuperscript{5,21}. The higher order correlation memory effects lead, in this approximation, to an effective reduction of the site density after the first jump. In the present language the Scher-Lax theory is equivalent to keeping no memory of previous jumps at all i.e. rerandomising after every step. The exact treatment of 3-site processes is essential for the Hall-conductivity for $\sigma_{xy}(\omega)$ however, it turns out that the two-site selfconsistent theory is perfectly adequate. It is also interesting to note that our path summation approximations would be exact if the system were an infinitely coordinated a) Cayley tree b) triangular tree lattice. The two-site selfconsistent theory is summarized by the following set of equations

$$\sigma_{xx}(i\omega) = \frac{\hbar^2}{k_B T} n^2 \int \int \int \frac{\rho(E) \rho(E') R^2 dR dE dE'}{\left(\tau(E, E', R)\right)^{-1} + (i\omega F(E') + \sigma_1(E', i\omega))^{-1}}$$

(8)

where $\sigma_1(E', i\omega)$ satisfies the integral equation

$$\sigma_1(E', i\omega) = n_a \int \int \frac{\rho(E'') dR dE''}{\left(\tau(E', E'', R')\right)^{-1} + (i\omega F(E'') + \sigma_1(E'', i\omega))^{-1}}$$

(9)

and $n$ is the site density, $\rho(E)$ the normalized energy distribution function (density of states), $a_p$ is the density reduction factor due to closed loops \textsuperscript{21} $a_p = e^{-1}$. We have assumed a random spatial distribution of sites. The thermopower can be evaluated \textsuperscript{21} using the energy dependent conductivity $\sigma(E, 0)$. Considerable simplification is achieved if the jump rates $W_{ij}$ are symmetric, here we find

$$\sigma_{xx}(i\omega) = n_c (1 - n_c/n) \frac{\hbar^2}{k_B T} D(i\omega)$$

(10)

where $n_c$ is the density of carriers and $D(i\omega)$ the single particle diffusion coefficient given by

$$D(i\omega) = \frac{\hbar^2}{n^6} \int \frac{\rho(E) dR dE}{(W(E, R))^{-1} + (i\omega + \sigma_1(i\omega))^{-1}}$$

(11)

where

$$\sigma_1(i\omega) = n_a \int \frac{\rho(E) dR dE}{(W(E, R))^{-1} + (i\omega + \sigma_1(i\omega))^{-1}}$$

(12)

Equation (11) can also be written in the more elegant form $D(i\omega) = \frac{<R^2(i\omega)>}{\hbar^2} \sigma_1(i\omega)$ which then defines an effective mean squared hopping distance trivially obtainable using (11) and (12). A similar result has been derived by Gochancour et al. \textsuperscript{23} in connection with the exciton diffusion problem using a diagrammatic technique. Their result is identical to (11) and (12) if $a_p$ is taken as $a_p = 1/2$.

The frequency dependent Hall-conductivity in the 3-site selfconsistent description becomes\textsuperscript{22}
where $A_{ij}^{[H]}$ represents the first order modification of $\tau_{ij}^{[H]}$ in an interference process over an intermediate site "0" in a magnetic field. Again $\sigma_{xy}(i\omega)$ simplifies considerably for symmetric hopping frequencies. One then replaces $\bar{\sigma}_1(E,i\omega) + i\omega F(E_j) \tau_{ij}^{[H]}$, $F(E) \rightarrow 1$ and $T_{ij} \rightarrow W_{ij}$. In deriving $\sigma_{xy}(i\omega)$, we have made the usual assumption that 3-site hopping junctions (Hall triangles) dominate the Hall conductivity in the hopping regime. The above equations for $\sigma_{xx}(i\omega)$ and $\sigma_{xy}(i\omega)$ are completely general, they apply to any phase incoherent transport processes describable by the Master equation with no constraints on the hopping lengths. All one has to do is to substitute the corresponding "jump frequencies".

The frequency dependence of $\sigma_{xx}(i\omega)$ has a physically more transparent interpretation in time space. For simplicity we shall consider only the symmetric case, here we have

$$6D(t) = \frac{2}{\Delta t} < R^2(t) > = \frac{2}{\Delta t} \left[ \sum_{ij} R_{ij}^2 G_{ij}(t) \right]$$

(14)

The time dependent diffusion coefficient $D(t)$ defined by (14) is the inverse Fourier-Laplace transform ($F^{-1}$) of $D(i\omega)/\omega$. The frequency (time) dependence of $D(i\omega)$ therefore reflects the fact that the derivative of the mean-squared distance $< R^2(t) >$ moved by a particle is not a constant in a disordered system.

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Fig. 4: The conductivity $\sigma_{xx}(0)$ (left curve) and Hall mobility $\mu_H$ (right curve) plotted against $an^{-1/3}$ in the $\bar{R}$-hopping problem ($W_{ij} = V_o e^{-2aR_{ij}}$). Solid lines: present theory using eq. (10) and (13). The points are the numerical simulations due to McInnes and Butcher, and the dotted lines are theories due to the same authors. The curves marked BB and FP refer to the work in refs. (18) and (33) respectively, QCA is the diffusion equation approximation (ref. 22).
Defining the degree of dispersion \( d \) as \( d = \frac{\text{Re} \, D(\omega = \infty)}{\text{Re} \, D(\omega = 0)} \), then \( d > 1 \) in general and thus \( D(t) \) decreases with time eventually reaching a constant \( d.c \) value. At short times the diffusion is dominated by the well conducting clusters, in the long time limit, however, the particle must eventually see the slow conducting channels. The time dependence of \( D(t) \) is believed to be the cause of the so-called dispersive transport phenomenon, which can also be produced by diagonal disorder, i.e. trapping and release of particles. The degree of dispersion is dependent on the model considered. In some models \( D(t) \) can in fact vanish, a situation referred to as quasi-localisation. One should note that our conductivity equations are exact in the high frequency and high density limits, in each case we obtain the diffusion equation limit, for example

\[
\sigma_{xx} = \frac{e^2}{kT} < \sum \frac{R_{ij}}{t_{ij}} >.
\]

Application to hopping transport. - We have analysed the validity of our approximation for \( \sigma_{xx}(\omega) \) by comparing our results with the computer simulations of the R-hopping problem by McInnes and Butcher. Here we simply have \( W_{ij} = \nu_0 \, e^{-2a[R_{ij}]} \), the rates are symmetric and the appropriate equations are (11) and (12). The simulation results are compared with \( \sigma_{xx}(0) \) in fig. (4). The agreement is excellent for all values of the effective density parameter \( \alpha \). The frequency dependence \( \text{Re} \, \sigma_{xx}(\omega) \) is shown in fig. 5a-c. At higher densities \( \alpha > 5 \), both the Scher-Lax and our theory are in good agreement, for low densities the Scher-Lax low frequency results begin to deviate quite strongly as expected. The a.c conductivity follows an \( \omega^s \) law with \( s \) decreasing with increasing "density" \( n^{1/3} \). The reason is that with increasing \( n \) the spatial disorder decreases, eventually the system becomes a "homogeneous liquid".

The d.c Hall mobility \( \mu_H = \frac{\sigma_{xy}(0)}{\sigma_{xx}(0)} \) is shown in fig. (4). The theoretical curve using (13) with the symmetric R-hopping frequencies is in good agreement with the computer points due to McInnes and Butcher. At low densities our results agree with the percolation approach of McInnes and Butcher, Böttger and Bryksin (except for the prefactor) but deviate from those of Pollak and Friedman. In the percolation approach one has to limit the size of the contributing "Hall triangles" and this has been the subject of some controversy. Friedman and Pollak cut off the lengths by using the first nearest neighbour distribution function. The selfconsistent equation (13) however tells us without further assumption that the cut-off occurs at the critical hopping distance...
This is the reason for the discrepancy. Unfortunately no computer points are available in this region of density to check these predictions and conclude the discussion. The Hall mobility including spatial and energetic disorder has recently been evaluated by Gr"unevaid et al. using percolation theory.

Consider now hopping at the Fermi level. The rates $\tau_{ij}$ are here the Ambegaokar-Halperin-Langer rates

$$\tau(E,E',E) = v_0 e^{-2\alpha |R_{ij}|} \cdot \exp[-(|E| + |E'|-|E-E'|)/2k_BT]$$

and $\sigma(E,\omega)$ has to be solved using the integral equation (9). Numerical solutions show that it is quite permissible to work with the simpler symmetric theory and to interpret the energy dependence as due to symmetric barriers. Writing therefore

$$W_{ij} = v_0 e^{-2\alpha |R_{ij}|} - |E|/k_BT,$$

and substituting this in (9) for a constant density of states $\rho$, we obtain at low temperatures

$$1 = \frac{4T}{T_0} \int \frac{x^2}{e^{x\sigma_1(0)} + 1}$$

which for $T<<T_0$ gives us Mott's law $\sigma_1(0)=v_0 e^{-(T_0/T)^{1/4}}$ with $T_0=\eta(T_0/T)^{1/4}$, the critical hopping time. Whether transport is

$$D(\omega/\nu)$$

lattice as an infinitely coordinated Cayley tree, where $a_p=1$. The path summation approximation is less good in 2 dimensions, but excellent results for the d.c and a.c conductivity are obtained if one identifies $a_p^{-1}$ with the corresponding percolation number $v_C$.

Turning to the frequency dependence, the numerical solution of $\Re \sigma_1(\omega)$ is shown in fig. 6. The temperature dependence of the exponent $s$ in the $\omega^s$ region is simply a consequence of the fact that the dispersion $d$ decreases with temperature as it obviously must: with increasing $T$ the energetic disorder disappears. For a given $\omega$, $s$ decreases roughly linearly with $T$ when $\rho(E)$ is constant. In fact when $T<\omega$ and $n>\omega$, $s<0$, i.e. there is no frequency dependence in the diffusion equation limit. In time space $D(t)$ behaves as $t^s$ initially, and reaches the d.c value when $t=t_c$ where $t_c=v_0^{-1} \sigma(\nu_0/T)^{1/4}$, the critical hopping time. Whether transport is
dispersive or not therefore depends in the hopping model on the time scale of the experiment in relation to $t_c$. For sufficiently short times $D(t)$ will always be time dependent in a disordered system.

Application of the theory to experiments on amorphous materials poses some very serious problems. Fig. (7) is a comparison of Re $D(\omega)$ with a set of data by Long and Balkan. The fit to the frequency dependence is perfect however two problems arise: the theoretical d.c. value is two to three orders of magnitude too small. Even if one discards this discrepancy, the required value of $\nu_0$ is unreasonably large ($\nu_0 \sim 10^{12}$ s$^{-1}$) in the framework of the hopping theory, very large values of $\nu_0$ in the range $[10^{16} - 10^{25}$, s$^{-1}]$ and large variations in this number because annealing and preparation cause $\sigma_{xx}(0)$ to change by many orders of magnitude whereas the value of $T_0$ hardly changes at all. The above observation is therefore an example of a more fundamental difficulty not connected with any theoretical approximation, but rather to the fact that our basic understanding of the fundamental hopping process in amorphous semiconductors is still incomplete. The dilemma is that on the one hand so many qualitative features of the hopping model seem to fit with observation (i.e. the $T^{1/4}$ law, the $\omega^5$ dependence and the temperature dependence of $s$) and on the other hand that the absolute values and numbers cannot be explained on the basis of the simple Miller-Abrahams hopping rates.

**Diffusion and relaxation.** - Let us now extend the diffusion theory to treat relaxation problems. In the electronic and nuclear spin-relaxation problem, one is interested in the time decay of the longitudinal magnetisation. We consider therefore symmetric jump frequencies and let $p_i(t) = [n_i^+(t) - n_i^-(t)]$ be the local magnetisation at the site "i". This obeys the linear Master equation

$$\frac{dp_i(t)}{dt} = \sum_j W_{ij}^+ p_j(t) - \sum_j W_{ij}^- p_j(t) - \delta_i (p_i(t) - p_0) - 2A p_i(t)$$

where $p_0$ is the equilibrium value and $2A$ the spin-flip rate due to an external r.f field. The decay of the average magnetisation $p(t)$ per site or more generally, the number of excitations surviving at time $t$, can be evaluated using ($p_0 = 2A = 0$),

$$p(t) = \langle \sum_j G_{ij}(t) \rangle$$

where $G_{ij}(t)$ is the probability function in the presence of loss terms. Before attempting to evaluate $G_{ij}(t)$, we have to distinguish two physically different situations: a) the loss rates $\delta_i$ are local i.e. the effective range of a relaxation centre is less than the average intersite spacing. Here we can assume that the rates $\delta_i$ are distributed independently $p(\delta_1, \delta_2, ..., \delta_N) = p(\delta_1) p(\delta_2) ... p(\delta_N)$, remain in the localized or site representation and use standard scattering theory techniques for diagonal disorder in particular the well established Coherent Potential Approximation (CPA) $^{39,40}$, b) In the other limit, when the relaxation rate associated with a given centre is long ranged like for example in the model of nuclear spin-relaxation of paramagnetic impurities treated by de Gennes, it is advantageous to work in the continuum representation. In both the ESR and NMR problems of interest we can assume that we are in case a). For a more general discussion of diffusion and relaxation when the centres have long ranges see ref. (42). Applying the CPA to (18), we obtain

$$p(t) = \sum_j G_{ij}(t)$$

where $s(\omega)$ is a single-site frequency dependent relaxation rate. For an ordered network this is given by

$$s(\omega) = \sum_j G_{ij}^{-1} (\omega + s(\omega))$$

where $G_{ij}(\omega)$ is the local Green function of the ordered lattice and
and $\Sigma(i\omega) = G_{OO}^{-1}(i\omega) - i\omega$, in the EMA, the disordered network is obtained by replacing $\Sigma(i\omega)$ with $\delta_{ij}(i\omega)$. The EMA does not correctly treat relatively strongly isolated sites and clusters and therefore overestimates the long time decay of $p(t)$. The statistical weight of such configurations is small, it is therefore also a reasonable approximation in the present case and we find

$$s(i\omega) = x(i\omega) \left( \frac{i\omega}{1-x(i\omega)} + \frac{n}{1-x(i\omega)} \right)$$

(22)

It is evident that in general the decay of $p(t)$ is non-exponential. In the long time limit it is, however, exponential with a time constant

$$\frac{1}{\tau} = (1-x(O)) x(O) a^{-1} \sigma_{ij} \left( \frac{n}{1-x(O)} \right),$$

(23)

Applying this formula to hopping at the Fermi level at low temperature and identifying $\tau^{-1}$ with the spin-lattice relaxation rate $T_1^{-1}$ we obtain

$$\frac{1}{\tau_1} = (1-x(O)) x(O) a^{-1} v_0 \left[ e^{-\left(T_0/T_1\right)^{1/4}} \right]^\mu, \quad \mu = (1-x(O))^{1/4}$$

(24)

The relationship to (3) is apparent, although we have to remember that (24) is still a complicated selfconsistency equation because of the relation between $x(O)$ and $01(1-x(O))$. A particularly simple and instructive case is the "deep sink" model with $\delta = 0$ and $\delta_i = 0$ with probability $c$ and $1-c$ respectively. Here $x(O) = c$ and the relation $T_1^{-1} = \sigma_{ij} \mu$ follows with $\mu = (1-c)^{1/4}$. A more realistic model is to take $\delta_i = \sum_j Y_{ij}^2 w_{ij}$ where $Y_{ij}^2$ is the matrix element of the hopping induced spin-flip process. The quantitative evaluation of $T_1^{-1}$ is considerably more difficult because of the correlation between $\delta_i$ and $W_{ij}$. Furthermore one should include spin-diffusion as well as hopping motion. The qualitative conclusion is that in the hopping regime, the spin-relaxation takes place in the fast conductivity paths, in general the excitation does not need to take the critical hopping paths which determine the d.c. conductivity, and the experimental relation (3) expresses just that.

Application to NMR in a-Si:H.- We can apply this formalism directly to NMR in a-Si:H. The diffusion rates $W_{ij}$ are now the spin diffusion rates

$$W_{ij} = v_0 \frac{R_{ij}}{R_{ij}} \delta_{ij}, \quad \delta_{ij} = \frac{1}{20} \gamma_{ij}^2 T_2^2$$

(25)

Where $\gamma_N$ and $T_2$ are the nuclear gyromagnetic ratio and spin-spin relaxation times respectively. The model of Carlos and Taylor is specified by writing

$$\delta = \frac{\gamma_N^2 h_0 R_{ij} \tau_{ij}^2}{1 + \omega_0^2 \tau_{ij}^2}, \quad \tau_{ij} = \tau_0 e^{E_i/k_B T}$$

(26)

where $h_0^2$ is the mean-squared fluctuations field caused by the modulation of the dipolar interaction in a local mode activation energy $E_i$ and $\omega_0$ is the resonance frequency. For a constant distribution of $E_i$ in the range $[E_{max}, E_{min}]$ we can analytically evaluate $T_1(N)$ and find

$$\frac{1}{T_1(N)} = \frac{\gamma_N^2 h_0^2 k_B T}{(E_{max}-E_{min})} + 2 \left[ \tan^{-1} \left( \frac{\gamma_N^2 h_0^2 c_i}{2 \omega_0 \tau_{ij} E_{max}/kT} \right)^{1/2} - \tan^{-1} \left( \frac{\gamma_N^2 h_0^2 c_i}{2 \omega_0 \tau_{ij} E_{min}/kT} \right)^{1/2} \right]$$

(27)

where $\Delta = (4 \gamma_N^2 h_0^4 c_i^4 / \sigma_i^4) > 0$, and $\sigma_i = \frac{1}{20} \frac{\gamma_N^2 h_0^2}{\omega_0} T_2 n^2$. Here $n$ is the density of
hydrogen sites per cm$^3$ and $x$ is the concentration of relaxation centres. Taking the experimental parameters for $n$ and $v_0$ and the ones assumed by Carlos and Taylor ($T_{\text{max}} = 80$ K, $E_{\text{min}} = 25$ K, $\tau_0 = 10^{-6}$ s), one can reproduce the minimum found experimentally in fig. (3), but to obtain $T_{\text{f}}(\text{min}) \approx 0.25$ s requires $x \geq 0.1$ or in other words, that more than 10% of these hydrogen participate in local mode relaxation clusters. One should expect to see such clusters in the NMR spectrum, the ones observed however do not correspond to fast relaxing centres$^4$. There is obviously a problem here and the magnitude of $x$ casts some doubt on the relaxation mechanism for the nuclear spin proposed by Carlos and Taylor. It seems that more experimental and theoretical work is needed to clarify the situation.

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