# Self-consistent diffusion coefficients in nearly-one-dimensional paramagnets*

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We calculate the off-chain diffusion coefficients in nearly-one-dimensional paramagnets self-consistently. The problem is solved by using a simplified mode-coupling theory. The results can be used to interpret the electron-paramagnetic-resonance linewidth in these systems.

Magnetic resonance has proven to be a very powerful technique to study the relaxation dynamics of paramagnets. In particular, the one-dimensional magnets can be studied well in this way. The slow $k \approx 0$ modes determine the EPR spectrum of a one-dimensional Heisenberg magnet entirely.[1-4] Richards and Salamon[5] have shown that also in the case of a two-dimensional magnet the long-wavelength modes have a dominating influence on the ESR spectrum. The relative weight of the $k \approx 0$ modes in a three-dimensional magnet can be neglected and all the modes contribute. The one dimensionality of a Heisenberg magnet is determined by the ratio of the interchain exchange and intrachain exchange constants. Actually, the one dimensionality of a paramagnet, as far as magnetic resonance is concerned, is determined by the ratio of the off-chain and intrachain diffusion constants. Hennessy, McElwee, and Richards[6] were the first to show that off-chain relaxation is faster than one would expect on the basis of a simple calculation based on moments. However, the off-chain spin motion was calculated with a Kubo and Tomita-type theory[7] and turned out to be nondiffusive. Reiter[8] has indicated that the calculation should be done self-consistently, and he showed that in that case the off-chain spin motion was diffusive. His numerical calculation was questioned because of the many approximations that were made.[9] From this it can be concluded that more reliable off-chain diffusion coefficients are needed.

We have calculated off-chain diffusion coefficients self-consistently for two cases: (i) a two-dimensional lattice; and (ii) a simple tetragonal lattice. These two models are of most interest from an experimental point of view. The calculation uses the Mori projection operator technique.[10] The self-energy $\Gamma(\vec{k}, z)$ is defined as the one-sided Fourier transform of the memory function $\Gamma(\vec{k}, t)$, which is defined by

$$\dot{\sum}(\vec{k}, t) = -\int_0^t \Gamma(\vec{k}, t-\tau) \sum(\vec{k}, \tau) d\tau , \qquad (1)$$

where

$$\sum(\vec{k}, t) = \langle S^z(\vec{k}, t) S^z(-\vec{k}) \rangle . \qquad (2)$$

The time dependence of $\Gamma(\vec{k}, t)$ is determined by a modified Liouville operator

$$\mathcal{L}' = (1-P)\mathcal{L}(1-P) \equiv Q\mathcal{L}Q , \qquad (3)$$

where $\mathcal{L}$ is the Liouville operator of the Heisenberg Hamiltonian, and in which the Mori projection operator $P$ is defined by

$$PX = \sum_{\vec{k}} S^z(\vec{k}) \langle S^z(\vec{k}) S^z(-\vec{k}) \rangle^{-1} (S^z(\vec{k}) | X) , \qquad (4)$$

in which the scalar product is defined by $(A|B) = \langle A^\dagger B \rangle$ and where $X$ is an arbitrary operator. If the equation of motion of $\sum(\vec{k}, t)$ is a diffusion equation for long times and long wavelengths, then

$$\lim_{k \to 0, z \to 0} \Gamma(\vec{k}, z) = D_1 k_x^2 + D_2 k_y^2 + D_3 k_z^2 . \qquad (5)$$

We have already limited ourselves here to lattices which do not allow cross terms to occur in Eq. (5). The formal expression for the self-energy is

$$\Gamma(\vec{k}, z) = i (Q\mathcal{L}S^z(\vec{k}) | [z - \mathcal{L}']^{-1} Q\mathcal{L}S^z(\vec{k}))$$
$$\times \langle S^z(\vec{k})S^z(-\vec{k}) \rangle^{-1} . \qquad (6)$$

If one wants to calculate $\Gamma(\vec{k}, z)$ from Eq. (6), one has to know the combination of four-spin correlation functions which occurs there. At this point we need an approximation for the self-energy. The most popular approximation is to neglect the operator $P$ and to decouple the correlation functions simultaneously. This approximation is known as the independent mode approximation (IMA) and the resulting equations of motion are the mode-coupling form.[11] This approach seems somewhat arbitrary although it can be given a solid basis in terms of diagrammatic expansions.[12] It is possible to construct diagrams which give all the moments correct to order $c^{-1}$, $c$ being the number of nearest neighbors. The lowest-order result, which is a partial summation of these diagrams (the bubble approximation), is equivalent to the mode-coupling theories.

At first sight one could think of alternative simplifications, for instance to neglect $P$ without de-

coupling. However, we will demonstrate that this leads to unphysical results. Using $Q\mathcal{L}S^z(\vec{k}) = \mathcal{L}S^z(\vec{k})$ for a paramagnet and neglecting $P$ in the propagator of Eq. (6) results in

$$\Gamma(\vec{k}, z) = i\,(\mathcal{L}S^z(\vec{k})|(z - \mathcal{L})^{-1}\mathcal{L}S^z(\vec{k}))$$
$$\times \langle S^z(\vec{k})S^z(-\vec{k})\rangle^{-1}\,. \qquad (7)$$

Equation (7) can be solved readily. Introducing the operator identity

$$\mathcal{L}(z - \mathcal{L})^{-1}\mathcal{L} = z^2(z - \mathcal{L})^{-1} - \mathcal{L} - z$$

in Eq. (7) gives

$$\Gamma(\vec{k}, z) = \frac{iz^2(S^z(\vec{k})|(z - \mathcal{L})^{-1}S^z(\vec{k}))}{\langle S^z(\vec{k})S^z(-\vec{k})\rangle} - iz\,. \qquad (8)$$

Using the one-sided Fourier transform of Eq. (1), one obtains

$$\Gamma(\vec{k}, z) = i\{z^2/[z + i\Gamma(\vec{k}, z)] - z\}\,. \qquad (9)$$

This has the unacceptable effect that $\Gamma(\vec{k}, z) = 0$, independent of $\vec{k}$. Retaining $P$ in the decoupled function is obviously wrong since this would prevent the two-spin correlation functions from decaying.

The conclusion is that the mode-coupling approach is one of the simplest nontrivial descriptions of spin dynamics. Within this approach the expression for the self-energy in the high-temperature limit becomes

$$\Gamma(\vec{k}, z) = [\tfrac{1}{3}S(S+1)]^{-1}\sum_{\vec{k}'}\,[J\,(\vec{k} - \vec{k}') - J(\vec{k}')]^2\int_0^\infty e^{izt}\langle S^z(\vec{k}', t)S^z(-\vec{k}')\rangle\,\langle S^z(\vec{k} - \vec{k}', t)S^z(\vec{k}' - \vec{k})\rangle\,dt\,, \qquad (10)$$

where $J(\vec{k})$ is the spatial transform of $J(r_{ij})$, the exchange interaction. Rather than solving Eq. (10) numerically exactly for anisotropic lattices, which is a formidable task, we will solve Eq. (10) approximately. Later on we will compare our results, where possible, with the full mode-coupling approach. We will assume that the two-spin correlation functions have a certain analytic form. As only adjustable parameters we introduce the

three diffusion coefficients $D_1$, $D_2$, and $D_3$. The limit

$$\lim_{k\to 0, z\to 0}\Gamma(\vec{k}, z)$$

can be calculated using Eq. (10), and since this limit is known [See Eq. (5)] self-consistent equations for the diffusion constants are acquired. The form we choose to be appropriate for the high-temperature two-spin correlation functions is

$$\langle S^z(\vec{k}, t)S^z(-\vec{k})\rangle = \tfrac{1}{3}S(S+1)\exp[(-D_1\sin^2\tfrac{1}{2}k_x a - D_2\sin^2\tfrac{1}{2}k_y b - D_3\sin^2\tfrac{1}{2}k_z c)4t]\,. \qquad (11)$$

First of all, we note that the expression has the correct behavior of spin diffusion for long terms and long wavelengths. The kinetic approach of Reiter[13] indicates that the simplest approximation for the self-energy which has the correct small-frequency behavior, is the supposition that the self-energy is proportional to the second moment. This is tantamount to assuming expression (11) to be valid. In addition, we want to point out that expression (11) can be obtained from a random walk picture of the dynamics. The most important aspect of assuming expression (11) is the fact that the diffusion constants can be calculated relatively simple. The self-consistent equations to be solved for a tetragonal lattice, with only nearest-neighbor exchange interaction, are

$$\frac{3D_1^2}{a^4} = S(S+1)J_1^2\int_0^\infty I_1(x)I_0^2(px)$$
$$\times x^{-1}\exp[-x(1 + 2p)]dx\,, \qquad (12a)$$

and

$$\frac{3pD_1D_2}{a^2b^2} = S(S+1)J_2^2\int_0^\infty I_1(px)I_0(px)I_0(x)$$
$$\times x^{-1}\exp[-x(1 + 2p)]dx\,, \qquad (12b)$$

where $p$ is defined as $D_2a^2/D_1b^2$, a measure for the one dimensionality of the diffusion process, $J_1$ is the exchange interaction along the chain, $J_2$ is the exchange constant perpendicular to the chain, and $I_n(\alpha)$ is the modified Bessel function of argument $\alpha$ and order $n$.[14] It is straightforward to derive the appropriate equations for the two-dimensional lattice from Eqs. (12a) and (12b). Equations (12a) and (12b) have been solved numerically. The major parts of the integrals were computed by analytic integration of expansions of the Bessel functions. The results are presented in Fig. 1.

Before we discuss the possible applications of these diffusion coefficients we would like to com-
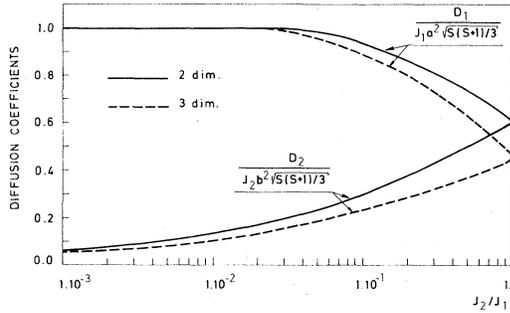
FIG. 1. Diffusion coefficients in anisotropic para-
magnets as a function of $J_2/J_1$. $J_2$ is the off-chain ex-
change interaction.

ment on the validity of our calculation with respect
to the full mode-coupling approach. The assump-
tion expressed in Eq. (11) describes only the long-
time and long-wavelength behavior correctly. We
expect the largest difference between our result
and the full mode-coupling approach to show up
for three-dimensional lattices and the smallest
difference for one-dimensional lattices. In one-
dimensional wave-vector sums the relative weight
of the $k \approx 0$ region is large and for these wave
vectors Eq. (11) is a good approximation. In
three-dimensional wave-vector sums all modes
contribute whereas Eq. (11) only describes the
longwavelengths correctly. Our value for the dif-
fusion coefficient in the case of the three-dimen-
sional simple cubic lattice is $0.26\, Ja^2\, [S(S+1)]^{1/2}$.
The numerical factor in the full mode-coupling
theory is 0.33,[15] which differs by $\approx 20\%$. We cal-
culate the diffusion coefficient for a square lattice
to be $0.34\, Ja^2\, [S(S+1)]^{1/2}$. To our knowledge, there
is no full mode-coupling solution for the square
lattice. Morita[16] finds $0.46\, Ja^2\, [S(S+1)]^{1/2}$ using
a stochastic assumption about the memory function.

The full mode-coupling diffusion coefficient in
one dimension is $1.39\, Ja^2\, [S(S+1)]^{1/2}$,[17] and our re-
sult is $0.58\, Ja^2\, [S(S+1)]^{1/2}$, which is surprising.
However, a check on the full mode-coupling calcu-
lation of the diffusion coefficient in one-dimension-
al paramagnets[17] shows that the original number
$0.69\, Ja^2\, [S(S+1)]^{1/2}$ is correct. This clarifies the
situation considerably because this differs from
our result less than 20%. It also shows that the
two-spin correlation functions obtained with the
mode-coupling theory are not as good as has been
claimed because the value of the diffusion coef-
ficient found with computer simulation of one-
dimensional spin dynamics is $1.32\, Ja^2 S$.[18] We
conclude that our results differ less than 20%
from the full mode-coupling solution which is very
gratifying. In the first place, because the mode-
coupling equations are not more accurate anyway,
and in the second place, our calculation is much

simpler. There is no reason to prefer perturba-
tion-type calculations for off-chain motion,[6]
which give unphysical nondiffusive motion, to the
mode-coupling approach. We claim that aniso-
tropic diffusion equations with the here-presented
off-chain diffusion coefficients are the most reli-
able descriptions of long-time off-chain motion
in nearly one-dimensional Heisenberg magnets up
to date. Before we turn to the possible applications
of the off-chain diffusion coefficients, we will com-
pare our results with the results of Reiter.[8] Our
calculations are valid in the complete range of $p$,
up to $p = 1$, and, in fact, they are the first calcula-
tions which cover this range. To what extent the
off-chain diffusion influences the on-chain diffusion
was not known before. In the range $0.001 < J_2/J_1$
$< 0.05$ the equation $D_2 = 0.51\ (J_2/J_1)^{1/3}\, J_2[\tfrac{1}{3}S(S+1)]^{1/2}$
gives a reasonable fit to the results for the tet-
ragonal lattice, and in the same range the equa-
tion $D_2 = 0.66\ (J_2/J_1)^{1/3}\, J_2[\tfrac{1}{3}S(S+1)]^{1/2}$ gives a rea-
sonable fit to the results for the two-dimensional
lattice. Reiter's result is $D_2 = 1.12\ (J_2/J_1)^{1/3}$
$\times J_2[\tfrac{1}{3}S(S+1)]^{1/2}$ for the three-dimensional case and
the two-dimensional case has not been calculated
before. In the indicated range of $J_2/J_1$, the differ-
ence in $D_2$ in the tetragonal lattice is not drama-
tic, but, as has been indicated, our results have
a firmer basis and are valid outside the in-
dicated range of $J_2/J_1$. The diffusion coefficients
calculated here are particularly useful for the
EPR absorption in paramagnets. The most direct
application is to the case of magnetically inequiva-
lent chains. These chains have different resonance
frequencies, and the magnitude of the interchain
coupling determines whether or not an exchange
averaged spectrum is observed. If an exchange
narrowed spectrum is observed, then the linewidth
depends in a very simple way on the off-chain dif-
fusion coefficients.[9] For treating equivalent chains
with interchain interactions one has to use the off-
chain diffusion coefficients in an ESR theory. For
this one can use the Kubo and Tomita theory[7] or
the theory of Reiter and Boucher.[2] In both cases
numerical evaluation will be necessary. This is
beyond the scope of the present paper since this
is only worthwhile doing if one wants to explain
the ESR characteristics of a specific compound.

We have presented in this paper the calculation
of off-chain diffusion coefficients in nearly-one-
dimensional Heisenberg magnets. The method
which has been used is a simplified version of the
mode-coupling approach, and the difference with
the full mode-coupling approach is estimated to be
less than 20%. The main application of the diffu-
sion coefficients will be the calculations of the
ESR linewidth in nearly-one-dimensional Heisen-
berg magnets.

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