Green's Function Calculation of

Effective Nuclear Relaxation Times in

Metals and Disordered Metals

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1 Introduction

The theoretical derivation of expressions for the magnetic nuclear relaxation times at very low temperatures and the description of the behaviour with temperature for such relaxation times, has been of major interest among the researchers in the field, specially because of the recent experimental possibility to obtain measurements of nuclear magnetic properties at such low temperatures. There has been a considerable amount of work in the area of nuclear magnetism [1], but a comprehensive theoretical interpretation of NMR relaxation times, at arbitrary temperatures, is still lacking. Recently, Shibata et al. has published a series of papers [2], [3] concerning the theoretical determination of the nuclear spin lattice relaxation time for a system of nuclear spins interacting with conduction electrons ina a metal. Using a theory of nonlinear spin relaxation [4], [5] they predicted a multiexponential spin-lattice relaxation behaviour.

In the case of disordered metals and high temperatures, where a Korringa law is aplicable, Warren [6] predicted an enhancement of the relaxation rate, which in some cases [7] could be as large as 6,500. More recently [8], Götze and Ketterle derived expressions for the Warren enhancement factor by means of normalized Kubo response functions [9].

In the present work, we make use of the two-times Green's function formalism in the regime of the Linear Response Theory to derive the temperature behaviour of nuclear relaxation times [10] for nuclei in metals and disordered metals. The results obtained are in complete agreement with those derived by Shibata in the assumption of an effective unique relaxation time [2], [3] and with experimental evidence [11], [12]. Also, there is agreement between our results and those derived by Götze and Ketterle [8] in the high temperature regime, where Korringa law is valid but additionally we obtained expressions for the enhanced relaxation rate which are valid in the whole temperature range. The organization of this paper is as follows, in section 2, the general formalism is derived, in section 3, we work out the Hamiltonian of the system from which the equation for the Green's function $<< I^0/I^0 >>_\omega$, which contains all the information relevant to the spin-lattice relaxation, is derived. This equation is then solved including terms up to second order in the electron nucleus interaction and the disorder parameters. Finally in section 4 we discuss the relaxation times formulas.

2 Green's Functions and the Relaxation Rate

We will consider a system which can be modelled by the total Hamiltonian:

$$H = H_S + H_{SL} + H_L \qquad (1)$$

where H_S represents the nuclear spin Hamiltonian, H_L is the Hamiltonian for the heat bath and H_{SL} represents the couplig between both systems, usually under the condition $H_L > H_S > H_{SL}$ which occurs commonly in NMR experiments. In order to consider the evolution of

the system toward thermal equilibrium, it is necessary to prepare the system in an initial non-equilibrium state. This can be achieved by the adiabatic switching on of a pertrubation, which in our case is a magnetic field along a particular direction, and suddenly at time t=0, this perturbation is switched off letting the system to evolve freely according to the Hamiltonian H. The perturbation can be written as:

$$H_1{}^t = - M . H_1{}^t \qquad (2)$$

where:

$$H_1{}^t = \theta(-t) \, e^{\varepsilon t} \, H_1 \qquad (3)$$

Within the linear response theory, the magnetization for t>0 is given by the following expression [13]:

$$< \delta M(t)> =$$
$$- \int_{-\infty}^{+\infty} << M(t);M(t')>>^{(-)} . H_1{}^{t'} \, dt' \qquad (4)$$

which is written in terms of the two times retarded Green's function. By using the causality property [13] of the retarded Green's function, it is posible to write the equation for the displacement of magnetization from the equilibrium situation as:

$$< \delta M(t)> =$$
$$- \frac{1}{2\pi} \int_{-\infty}^{+\infty} \frac{<< M;M>>_\omega^{(-)} . H_1}{i\omega + \varepsilon} e^{-i\omega t} \, d\omega \qquad (5)$$

where $< \delta M(t)> = <M(t)> - <M>_o$. It can be shown that:

$$< \delta M(t=0)> = - << M;M>>_o^{(-)} . H_1 \qquad (6)$$

so that taking the Laplace transform of eq. (5), it can be written as:

$$< \delta M(z)> = f(z) . < \delta M(t=0)> \qquad (7)$$

where:

$$f(z) = - \frac{1}{2\pi} \int_{-\infty}^{+\infty} \frac{G_M(\omega) . G_M^{-1}(0)}{(\omega - i\varepsilon)(\omega - iz)} \, d\omega \qquad (8)$$

with $G_M(\omega) = << M;M>>_\omega^{(-)}$.

We are interested in the asymptotic behaviour of $< \delta M(t)>$ since in that regime is that the relaxation rates are experimentally measured. According to Tauber's theorem [14], [15] an asymptotic espansion of f(t) can be written as:

$$f(t) = \sum_v e^{z_v t} \sum_{k=0}^{\infty} C_k{}^{(v)} \, \Gamma^{-1}(- n_k{}^{(v)}) \, t^{-(1+ n_k{}^{(v)})} \qquad (9)$$

where z_v represents the poles of the function f(z), $n_k{}^{(v)}$ the order of the pole and $C_k{}^{(v)}$ the coefficient in a Laurent expansion of f(z) around the pole. In the particular case of f(z) having only first order poles, eq. (9) can be written:

$$f(t) = \sum_v C^{(v)} \, e^{z_v t} \qquad (10)$$

Let us suppose that the Green's function can be written in the general form:

$$G_\alpha(\omega) = \frac{\sigma_\alpha(\omega)}{\omega - \alpha\omega_0 - W_\alpha(\omega)} \qquad (11)$$

where σ_α and W_α are complex functions. According to eq. (8) the poles of the function f(z) are related to the poles of the Green's function so that only those poles that are located at the upper complex plane must be considered [16]. In general it is necessary to make a complete analysis of the pole structure of the Green's function at the upper complex plane in order to describe the total aymptotic behaviour of the function f(t). As a simplifying assumption, we will consider the following zeroth-order approximation to the pole structure. We will first assume that the function $\sigma_\alpha(\omega)$ does not contribute with any pole. This

analyzed with some care. Secondly that the function W_α can be approximated by its value at the frequency $\alpha\omega_0$. This second assumption ussually is a very strong one since the whole pole structure is sometimes collapsed to a single first order pole, but nevertheless in many cases, this approximation gives the right relaxation behaviour correlating quite well with the experimental results. The relaxation rates obtained under this assumptions can be written in terms of the imaginary part of the function W_α evaluated at the frequency $\alpha\omega_0$, that is:

$$\frac{1}{T_1} = - \text{Im} \, W_0(0) \qquad (12)$$

and:

$$\frac{1}{T_2} = - \text{Im} \, W_+ \, (+\omega_0) = - \text{Im} \, W_- \, (-\omega_0) \qquad (13)$$

3 Hamiltonian and Equation for the Green's Function $G_0(\omega)$.

For the system considered in this work, the Hamiltonian can be written as in equation (1) where the different terms are:

$$H_Z = - \gamma \frac{h H_0}{2\pi} I^0 \qquad (14)$$

$$H_{SL} = C \sum_{v\,v'\,k\,k'} \Psi^+_{v'\,k'} \cdot \Psi_{v\,k} \times$$

$$\times \, [\frac{1}{2} I^0 (a^+_{v'\,k'+} \, a_{v\,k+} - a^+_{v'\,k'-} \, a_{v\,k-}) +$$

$$+ \frac{1}{2} I^+ \, a^+_{v'\,k'-} \, a_{v\,k+} + \frac{1}{2} I^- \, a_{v'\,k'+} \, a_{v\,k-} \,] \qquad (15)$$

with:

$$C = \frac{8\pi}{3} \gamma_e \gamma (\frac{h}{2\pi})^2 \qquad (16)$$

The lattice Hamiltonian can be written as the sum of two terms [8]:

$$H_L = \sum_{v\,k\,s} \varepsilon_v (ks) \, a^+_{v\,k\,s} \, a_{v\,k\,s} +$$

$$+ \sum_q \rho^+ (q) \, U(q) \qquad (17)$$

where:

$$\rho(q) = \sum_{ks} a^+_{k-\frac{q}{2}\,s} \, a_{k+\frac{q}{2}\,s} \qquad (18)$$

and represents the electron density fluctuations for wavevector q. The disorder in the lattice is represented by the Fourier transform U(q) of the random potential. This coefficient satisfies the symmetry property:

$$U^*(q) = U(-q) \qquad (19)$$

The equation for the Green function $G_0(\omega)$ is:

$$\hbar \omega G_0(\omega) = \frac{C}{2} \sum_{kk'} \Psi^+_k \cdot \Psi_k \, (<<I^+ \, a^+_{k-} \, a_{k+} \, ; I^0>>_\omega -$$

$$- <<I^- \, a^+_{k+} \, a_{k-} \, ; I^0>>_\omega) \qquad (20)$$

which is to be considered the root of an infinite set of hierarchy equations, that can only be decoupled by introducing some approximations. First, we will assume that there is no correlation between the electron operators and the nuclear spin operators. The second approximation will be a perturbative one, we will take into account only terms independent of U(q) in order to have an approximation for the root Green's function up to second order. Then the equation for the root Green's function can be written simply as:

$$\left\{ \hbar \omega - W(\omega) \right\} G_0(\omega) = F(\omega) \qquad (21)$$

where:

$$W(\omega) = \frac{C}{2}\sum_{kk'} \Psi_k^+ \cdot \Psi_k \times$$

$$\times \left\{ \frac{H_k^{+,(0)}{}_{k+}(\omega)}{\Delta_{kk}^+ - \Lambda_{kk}^+} - \frac{H_k^{-,(0)}{}_{k-}(\omega)}{\Delta_{\bar{k}k}^- - \Lambda_{\bar{k}k}^-} \right\} \qquad (22)$$

and:

$$F(\omega) = \frac{C}{2}\sum_{kk'} \Psi_k^+ \cdot \Psi_k \times$$

$$\times \left\{ \frac{F_k^{+,(0)}{}_{k+}(\omega) + G_k^{+,(0)}{}_{k+}(\omega)G_T(\omega)}{\Delta_{kk}^+ - \Lambda_{kk}^+} \right. -$$

$$\left. - \frac{F_k^{-,(0)}{}_{k-}(\omega) + G_k^{-,(0)}{}_{k-}(\omega)G_T(\omega)}{\Delta_{\bar{k}k}^- - \Lambda_{\bar{k}k}^-} \right\} \qquad (23)$$

with:

$$H_k^{+,(0)}{}_{k+}(\omega) = +\frac{C}{2}\Psi_k^+ \Psi_k \cdot \times$$

$$\times \left\{ n(k'-)(1 - n(k+)) + n(k+)(1 - n(k'-)) \right\} \qquad (24)$$

$$F_k^{+,(0)}{}_{k+}(\omega) = \langle [I^+ a_k^+{}_{-} - a_{k+}, I^0] \rangle_0 \qquad (25)$$

$$G_k^{+,(0)}{}_{k+} = \frac{C}{2}\Psi_k^+ \Psi_k \cdot [n(k'-) - n(k+)] \qquad (26)$$

$$G_T(\omega) = \langle\langle I(I+1) - I^{02}; I^0 \rangle\rangle_\omega \qquad (27)$$

$$\Delta_{kk}^+ = \hbar(\omega - \omega_0) + \varepsilon(k'-) - \varepsilon(k+) \qquad (28)$$

$$\Lambda_{kk}^+ = \sum_{q>0} |U(q)|^2 \left\{ \frac{1}{\Delta_{k',k-q}^+} + \frac{1}{\Delta_{k+q,k}^+} \right\} \qquad (29)$$

As it was discussed previously [17], the longitudinal relaxation rate is proportional to the imaginary part of the function $W(\omega)$. If it is taken into account that Λ is a complex function:

$$\Lambda_{kk}^+(\omega) = \mathrm{Re}\,\Lambda_{kk}^+(\omega) - i\,\mathrm{Im}\,\Lambda_{kk}^+(\omega) \qquad (30)$$

where:

$$\mathrm{Re}\,\Lambda_{kk}^+(\omega) = P\sum_{q>0} |U(q)|^2 \left\{ \frac{1}{\Delta_{k',k-q}^+} + \frac{1}{\Delta_{k+q,k}^+} \right\} \qquad (31)$$

and:

$$\mathrm{Im}\,\Lambda_{kk}^+(\omega) = \pi\sum_{q>0} |U(q)|^2 [\delta(\Delta_{k',k-q}^+) +$$

$$+ \delta(\Delta_{k+q,k}^+)] \qquad (32)$$

Equation (31) represents the dynamical shift in electronic energy due to the disorder and equation (32) corresponds to the electronic relaxation rate function, which in the limit of $\omega \to 0$, gives the electronic relaxation rate $1/\tau_e$. The imaginary part of $W(\omega)$ now becomes:

$$\mathrm{Im}\,W(\omega) = \frac{C^2}{4}\sum_{kk'} |\Psi_k|^2 |\Psi_{k'}|^2 \times$$

$$\times \left[\left\{ \frac{n(k'-)(1-n(k+)) + n(k+)(1-n(k'-))}{(\Delta_{kk}^+ - \mathrm{Re}\,\Lambda_{kk}^+)^2 + (Im\,\Lambda_{kk}^+)^2}\,\mathrm{Im}\,\Lambda_{kk}^+ \right\} + \right.$$

$$\left. + \left\{ \frac{n(k'+)(1-n(k-)) + n(k-)(1-n(k'+))}{(\Delta_{\bar{k}k}^- - \mathrm{Re}\,\Lambda_{\bar{k}k}^-)^2 + (Im\,\Lambda_{\bar{k}k}^-)^2}\,\mathrm{Im}\,\Lambda_{\bar{k}k}^- \right\} \right] \qquad (33)$$

In the case of a perfect metal, that is for $U(q) = 0$, we get from equation (33), the following expression for the relaxation rate [17] :

$$\frac{1}{T_1} = \frac{\pi^2 C^2}{h} \sum_{kk'} |\Psi_k|^2 |\Psi_{k'}|^2 [n(k+)(1-n(k'-)) + $$
$$+ n(k'-)(1-n(k+))] \delta(\Delta_{kk'}) \qquad (34)$$

which exhibits a Korringa behaviour at high temperatures and attains a maximum for the relaxation time at very low temperatures, comparable with nuclear spin energies [17]. in the case of disorder we get for the relaxation rate:

$$\frac{1}{T_1} = \frac{\pi C^2}{2h} \sum_{kk'} |\Psi_k|^2 |\Psi_{k'}|^2 \times$$

$$\times [\left\{ \frac{n(k'-)(1-n(k+)) + n(k+)(1-n(k'-))}{(\Delta_{k'k} - \text{Re}\,\Lambda_{k'k}^+)^2 + (\text{Im}\,\Lambda_{k'k}^+)^2} \text{Im}\,\Lambda_{k'k}^+ \right\} +$$

$$+ \left\{ \frac{n(k'+)(1-n(k-)) + n(k-)(1-n(k'+))}{(\Delta_{k'k} - \text{Re}\,\Lambda_{k'k}^-)^2 + (\text{Im}\,\Lambda_{k'k}^-)^2} \text{Im}\,\Lambda_{k'k}^- \right\}]$$

$$(35)$$

in the limit ω goes to 0.

4 Conclusions

In the whole temperature range, equation (34) can be calculated numerically, and the result for the case of a perfect metal was obtained in reference 17, where it can be appreciated that T_1 shows a maximum at a temperature that is approximately half of the nuclear spin temperature, which is consistent with the result obtained by Shibata and co-workers in the supposition that the relaxation process can be described by a unique effective relaxation time T_1 as the observed experimental behaviour is. Also there is a correspondence between both results in the limit of low temperature, leading us to think that our calculation, even in its simpler approximation, is quantitatively correct. From the experimental point of view there are not enough data to decide whether a single or a multiexponential relaxation takes place, but the general tendency is to believe that even though the process seems actually to be multiexponential, it could be described by an effective relaxation time T'_1, which is the time that characterizes the evolution of observables, in particu-

lar, the longitudinal magnetization [11], [12]. The temperature dependence shown experimentally by this time T'_1, agrees completely with the behaviour calculated in reference 17. Also, equation (35) takes into account the enhancement of the relaxation rate for the whole temperature range, showing at high temperatures a departure from Korringa's law proportional to the electronic relaxation time as Warren proposed. The result obtained for the enhanced relaxation rate shows that this enhancement will be present even at low temperatures, as equation (35) is valid in the whole temperature range. The approximation assumed in this work, besides its simplicity, takes into account the main features present in the temperature behaviour of relaxation times, within the limits of Linear Response Theory, and it can be extended to consider more realistic models or systems.

Acknowledgments

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