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TWO PARTICLE VERSUS THREE PARTICLE CONTRIBUTIONS TO A DYNAMICAL CORRELATION FUNCTION IN LIQUIDS

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Abstract - That part of nuclear spin relaxation rate in a liquid which is caused by electric interaction with neighbour particles, \( R_Q \), is determined by the sum of a two particle and a three particle correlation function. In order to explain the weak temperature dependence generally found in pure liquid metals, we present and discuss a simple model description for the time development of the first neighbour shell. Two- and three-particle terms cancel in liquid metals for intermediate and long times, leading to a short correlation time. This is in agreement with the general trend of \( R_Q \) data and with recent thorough theoretical treatments of a particular case.

I - INTRODUCTION

While bonding interactions of each constituent atom with its neighbours are strong, and thus multiple correlations are essential, in any liquid or amorphous system, it is rather for weak interactions that one can single out one process and separate the contributions made by two-particle and by higher terms. One such case is nuclear spin relaxation in liquids /1/ by quadrupolar (i.e. electric) interaction with neighbour particles. It is caused by the fluctuations of the electric field gradient (efg) at the probe (p) nuclear site. The efg leads to a short ranged interaction between the probe's nuclear quadrupole moment \( Q \) and the neighbour \( i \), certainly so in metallic, i.e. electronically shielded systems which will concern us as examples. For the situation in ionic liquids, see e.g. /2/. One may then restrict oneself to the nearest neighbours. The efg component \( V^m_2 \) is a sum of contributions over all (nearest) neighbours, and the nuclear spin relaxation rate \( R_Q \) is proportional to the time integral of the efg correlation function \( c_{efg} \):

\[
R_Q = f(I, k) \cdot (eQ/M)^2 \cdot \int c_{efg}(t) \, dt
\]

\[
c_{efg}(t) = \sum_{m=-2}^{2} V^m_2(0) \cdot V^m_2(t) >
\]

\[
V^m_2(t) = \sum_i v_i(r_{ip}(t)) \cdot \sqrt{4\pi} \cdot \chi^{m}_2(\theta_{ip}(t), \phi_{ip}(t))
\]
The sum over \( i \) runs over the neighbours, \( k \) is the multipole order observed (\( k=1 \) in NMR, \( k=2 \) in TDPAD). We shall assume that the efg function \( v_i(r_{ip}) \) can be derived from an effective interatomic potential \( \tilde{V}_i(r_{ip})/3, 4/ \). It is the distance \( \vec{r}_{ip} = \vec{R}_p - \vec{R}_i \) which through (1) - (3) occurs twice in \( R_Q \), thus introducing four position vectors \( \vec{R}_p(0), \vec{R}_p(t), \vec{R}_i(0), \) and \( \vec{R}_i(t) \) or \( R_j(t) \). Similar expressions occur for broadening of 4f ionic levels, or in light scattering from interaction polarized atoms, e.g. liquid Ar.

It is unfavourable that the direct information about \( R_i \) or \( f \)'s is averaged out in the observable quantity \( R_Q \), this being a time and thereby a space integral. The advantage of \( R_Q \) is however that it can be measured by NMR in quite a few liquids, viz. if they have a spin 1/2 nucleus, notably liquid metals /5/, /6/ like Cu, Ga, Ge, Rb, In, Sb, Hg, Bi and alloys of these. Even more systems become accessible by using excited nuclear states and TDPAD technique (see e.g. /7/). An important general trend pointed out by Titman et al. /6/ is that \( R_Q \sim 1/\sqrt{T} \) in all pure liquid metals studied so far.

For one model case, Rb, a thorough theoretical treatment has recently been given by Bosse et al. /4/. Also, the earlier theories for \( R_Q /8/ \) by Sholl, and by Warren have very recently been improved by Gaskell and Woolfson /5/ in such a way as to reconcile short-time and long-time behaviour of \( c_{\text{efg}}(t) \) while still starting from the Kirkwood superposition approximation for the three particle correlation function.

Since exact calculations are rather involved, it had appeared to us that for applications and extensions it might be helpful to develop a simple, clear and easily calculable model description /10/. Because of the isotropy in the liquid, (2) becomes

\[
f(I,k) = \frac{3}{80} k(k+1) \frac{41(I+1) - k(k+1) - 1}{I^2 (2I-1)^2} \tag{4}
\]

where \( \alpha_{ipj}(t) \) is the angle subtended by \( (\vec{r}_{ip}(0), \vec{r}_{jp}(0)) \). (5) is a sum of a two- and three particle term. They compensate to a large extent if \( v_i = v_j = v \) as in pure metals /8/, /4/, /9/. In order that the model calculation treat the compensation realistically, we assume that the n.n. have at \( t=0 \) an average arrangement around the probe atom with \( <v>^I_{2}(0)>0 \). The dependence of \( c_{\text{efg}}(t) \) on the angular motion is neglected because the variation of \( v \) due to radial motion is much stronger. One may then choose cubic symmetry (like in a b.c.c. arrangement), where \( \sum_i P_i(\cos \alpha_{ipj})=0; \) this is the most restrictive assumption about three particle correlations being made here. Then \( T_2 \) and \( T_3 \) acquire opposite signs and simplify considerably:
$K$ is the number of nearest neighbors. The distribution function $W(r_0; r, t)$ gives the probability to find a neighbor atom at time $t$ between $r$ and $r + dr$, given that it was between $r_0$ and $r + dr_0$ at $t=0$. $g_0$ is the first peak of the static pair distribution $\Omega(0)$. Eqs. (6) contain the often stressed point /8/, /9/ that the power at which $g(r)$ appears is different in $T_2$ and $T_3$. The model chosen ensures that $R > 0$.

Apart from the angular restriction mentioned, we treat the dynamics of the neighbors independent from each other as the relative motion $\mathbf{p}_i$ in one dimension. According to Haan /11/ a good approximation for the relative motion of two neighbor atoms as described by $W(r_0; r, t)$ is obtained from Smoluchowski's diffusion equation

$$\frac{\partial W}{\partial \tau(t)} = D \{ \Delta W + \mathbf{V} \cdot \nabla \mathbf{W} \} \tag{7}$$

with an effective potential $\psi(r) = -k_B T \ln \, (g(r))$, and a nonlinear time scale /11/ which we approximated by $\tau(t) = t(1 - (1 - \exp(-\beta_1 t))/\beta_1 t))$ with $\beta_1 = 0.4 \, k_B T / m D$ according to the results of /11/. The Smoluchowski equation was carefully integrated numerically, and (6) was evaluated using various assumptions for $\mathbf{V}(r)$ of the form $\mathbf{V}(r) = Z/r \cdot \exp(-\lambda r)$ or $\mathbf{V}(r) = Z \{(\rho/r)^m - m/n \cdot (\rho/r)^n\}$. For $\rho$, the position of the maximum of $g_0(r)$ was taken, in order to stress compatibility of $g(r)$ and $\mathbf{V}(r)$.

The results show a characteristic difference in the time development of the two particle and three particle term, $T_2(t)$ and $-T_3(t)$ respectively, see fig. 1: Because the efg function $\mathbf{V}(r)$ decreases but $g(r)$ increases steeply with $r$, and they appear essentially as $<g \, \mathbf{V}^2 \, W>$ in $T_2$, but as $<g \mathbf{V} \cdot \mathbf{V} \mathbf{W}>$ in $T_3$, $T_2$ gives stronger weight to small $r$ ($<g$). In this region, relative motion is fast separation, so that $T_2(t)$ acquires an additional fast initial decay which essentially destroys the inevitable initial excess of $T_2(0)$ over $T_3(0)$. Apart from that, both $T_2(t)$ and $T_3(t)$ have a similar time dependence. Equality of the potential $\psi(r)$ and $\mathbf{V}(r)$ for $i$ and $j$ makes $T_2(t)$ and $-T_3(t)$ coincide for large $t$ where they are diffusion controlled. The characteristic decay times $\tau_{2,3} = \int T_{2,3}(t) dt / T_{2,3}(0)$ differ by an order of magnitude from $\tau = \int (T_2(t) + T_3(t)) dt / (T_2(0) + T_3(0))$, independent of $\mathbf{V}(r)$.

Since $R_0 \sim \int (T_2 + T_3) dt$, it is dominated by the short correlation time of the compensation between $T_2$ and $T_3$, and so is its temperature dependence which thus becomes weak, see fig. 2. The compensation effect has singled out a part of the efg correlation function. It decays fast as suspected originally /6/ from considering the free gas limit. The results from the present model calculations are in full agreement with those of the much more elaborate theoretical treatment for Rb by /4/, which employ
Fig. 1 - Normalized efg correlation functions: two particle contribution $T_2(t)/T_2(0)$, magnitude of three particle contribution $-T_3(t)/T_2(0)$ and $c_{\text{efg}}(t)/T_2(0)$ (dashes, dash dot, and full line, respectively). Parameters are for liquid Ga at its melting point $T_m = 323$ K, with $V(r) = Z/r \exp(-2.0 \cdot r/\bar{A})$. Note that here $T_3(0)$ cancels more than 60% of $T_2(0)$. One obtains $\tau_3 = 1.98$ ps, $\tau = 0.36$ ps for the correlation times.

mode coupling theory and molecular dynamics, and with a similar calculation for Ga /12/. They also agree with the recent calculations by Gaskell and Woolfson /9/ where it turns out again that in the pure liquids considered (Rb, Ne) the small short-time surplus of the two-particle over three-particle contribution is decisive. When speaking of two particle term it is to be kept in mind that here the distance vector, taken at two times, enters, not the position vectors. - The present curves for $T_2(t), T_3(t)$ are definitely smoother than those of Bosse et al. or Gaskell and Woolfson probably because of the use of the Smoluchowski equation.

Further development of the use of $R_Q$ for studying dynamics in liquids may start from the fact that the relative importance of $T_2$ and $T_3$ can be varied. This is achieved by choosing partners A, B for which the efg functions $v_{A}, v_{B}$ are different. Then an increase of $R_Q$ over $c_A \cdot R_{QA} + c_B \cdot R_{QB}$ develops which is proportional to the three particle term $T_3/10/$. This point will be discussed in a subsequent paper (R. Brinkmann et al. to be published). However, when A-B bonding becomes much stronger than A-A, B-B bonding, $R_Q$ is determined by the A-B, i.e. two particle correlations /13/.

- We conclude by repeating that quite a lot of data has been accumulated on $R_Q$ of liquid alloys (/5/, /7/, see also /14/). Quantitative and reliable efg functions $v(r)$ are, however, still lacking. Once given these, one should be able to extract from the data quantitative information about dynamics of two- and three-particle correlations, including their change upon alloying, in quite a few metallic liquids.
Fig. 2 - Temperature dependence of the correlation time $\tau$ of the efg correlation function, with parameters for liquid Ga with $V(r) = Z/r \exp(-1.5 r/\AA)$. For comparison, $\tau \propto T^{-1/2}$ (ref. /6/)), and $\tau \sim D^{-1}$ (see ref. /8/) are included. (To complete the discussion of the temperature dependence of $R_Q$, the moderate increase of $c_{efg}(0)$ with $T$ has to be included, see e.g. /4/.)

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