TEMPERATURE DEPENDENCE OF QUADRUPOLAR RELAXATION RATE IN LIQUIDS

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Abstract.- A mode-coupling approximation is proposed to calculate the fluctuation spectrum of the electric field-gradient at the site of a probe atom. The theory is applied to compute the quadrupolar relaxation rate in liquid gallium as a function of temperature.

Theoretical framework: The quadrupolar relaxation rate is determined by the low-frequency limit of the spectrum of field-gradient fluctuations at the nuclear site /AbrP 53/. We write

$$R_Q(T) = \text{const.} \langle |V_0^{(2)}|^2 \rangle \tau_c(T) \quad , \qquad (1)$$

where the constant is fixed by nuclear quadrupole moment and spin, and $V_0^{(2)}$ denotes a spherical component of the field-gradient tensor. The correlation time

$$\tau_c(T) = [K''(\omega = 0)]^{-1} \qquad (2)$$

is expressed in terms of the memory kernel $K''(\omega)$ defined by

$$\int_{-\infty}^{+\infty} \frac{dt}{2} e^{it\omega} \frac{\langle V_0^{(2)}(t)^* V_0^{(2)} \rangle}{\langle |V_0^{(2)}|^2 \rangle} = \frac{K''(\omega)}{[\omega + \fint \frac{d\varepsilon}{\pi} \frac{K''(\varepsilon)}{\varepsilon - \omega}]^2 + [K''(\omega)]^2} . \qquad (3)$$

We apply Sholl's model /Sho 67/ approximating

$$V_0^{(2)} \approx \int d\vec{r}^3 \int d\vec{r}^{3\prime} u_0^{(2)}(\vec{r} - \vec{r}') \rho_0(\vec{r}) \rho(\vec{r}') \qquad (4)$$

with the spherical component $u_0^{(2)}(\vec{r})$ of the effective field-gradient at the probe position $\vec{r}$ due to a liquid particle at $\vec{r} = \vec{0}$; $\rho_0(\vec{r})$ and $\rho(\vec{r})$ denote the density of probe- and liquid particles at $\vec{r}$, respectively. The effective potential $u(r)$ is assumed a known function of r independent of temperature.

Within the model eq. (4) the static field-gradient correlation $\langle |V_0^{(2)}|^2 \rangle$ is simply expressed in terms of the effective potential $u(r)$, the pair-correlation function $g_0(r)$, and the triplet-correlation function $g_0(r; r'; |\vec{r} - \vec{r}'|)$.

For calculating the dynamic correlation function eq. (3), we propose a mode-coupling approximation /BGZ 78, BGL 78/ for the memory kernel

$$K''(\omega) \approx K_L''(\omega) + 2K_T''(\omega) \quad , \qquad (5a)$$

$$K_{L,T}''(\omega) = \int_0^\infty dk\, k^2 W_{L,T}(k) \int_{-\infty}^{+\infty} d\varepsilon\, S_s(k;\varepsilon) \phi_{L,T}''(k;\omega - \varepsilon) , \qquad (5b)$$

which describes the coupling of the probe-particle motion ($S_s(k;\omega)$) to longitudinal <u>and</u> transverse current excitations ($\phi_{L,T}''(k;\omega)$). The vertex functions $W_{L,T}(k)$ measuring the strength of this coupling may be expressed in terms of $u(r)$ and $g_0(r)$.

Application to liquid gallium: The theory is applied to calculate the quadrupolar relaxation rate $R_Q(T)$, the static field-gradient correlation $\langle|V_0^{(2)}|^2\rangle$, and the correlation time $\tau_c(T)$ as functions of temperature for a Ga probe atom in liquid Ga using an effective potential $u(r)$ supplied by /Sho 74/ and/AppW 73/. The results are plotted in Figs. 1 and 2. While the

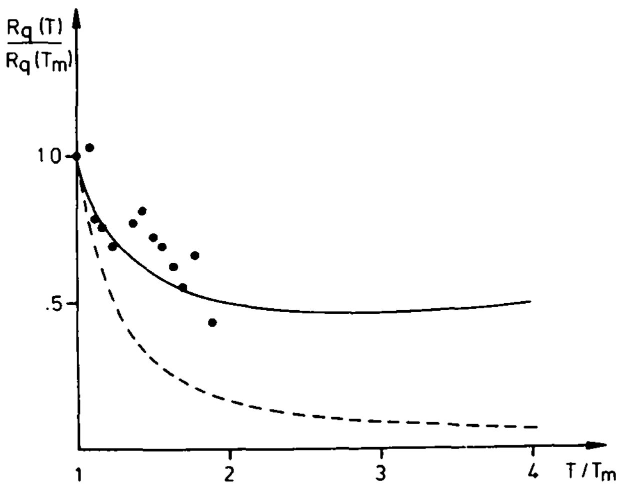

Fig.1: Temperature-dependence of quadrupolar relaxation rate in liquid Ga. Full line: Present theory; dots: experiment /CarH 76/; dashed line: simple diffusion model $R_Q(T) \propto D(T)^{-1}$

correlation time decreases with temperature T, the static correlation $\langle|V_0^{(2)}|^2\rangle$ is increasing function of T (Fig.2). From this behaviour of the factors in eq.(1), the variation of the quadrupolar relaxation rate with temperature (Fig. 2) can be inferred; $R_Q(T)$ is not only decreasing more slowly than predicted by the most simple diffusion picture but it will even increase slightly for $T \gtrsim 3T_M$.

To evaluate the quantities in Figs. 1 and 2 within Sholl's model, eq. (4), and the mode-coupling approximation, eq. (5), a series of additional, more technical approximations is necessary, because measurements of $g_0(r)$ /BizB 77/ are available for two temperatures T_1 , T_2 only (see table 1 below):

(1) Motivated by Kirkwood's superposition approximation /Kir 35/ we used $g_0(r;r';|\vec{r}-\vec{r}'|) \approx g_0(r)\,g_0(r')\,\Theta(|\vec{r}-\vec{r}'|-\sigma)$ in the calculation of $\langle|V_0^{(2)}|^2\rangle$. $\Theta(x)$ denotes the unit-step function and σ is defined below.

(2) Lacking extensive T-dependent measurements of the pair-correlation function, we used $g_0(r) \approx \exp[-v(r)/k_BT]$ with $v(r) = 4k_BT_M[(\sigma/r)^{12} - (\sigma/r)^6]$ and σ was chosen to correctly reproduce the peak position of $g_0(r)$ at $T = T_2$. This rather crude low-density approximation appears to be quite useful when applied in the calculation of vertex functions and static field-gradient correlations, where integrals of products of $g_0(r)$ with potential derivatives enter. Deviations of less than

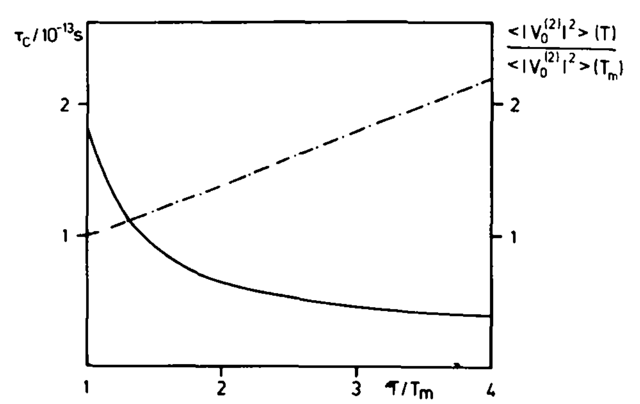

Fig. 2: Temperature-dependence of correlation time τ_c (full line) and static field-gradient correlations $\langle|V_0^{(2)}|^2\rangle$ (dash-dotted line).

30% were found when using the experimental $g_o(r)$ at the two temperatures available.

Table 1:

Parameters for Ga

T_M/K	303
$\sigma/Å$	2.48
$k_o/Å^{-1}$	2.50
$D_o/10^{-5}cm^2s^{-1}$	58.6
T_o/T_M	3.6
$n/Å^{-3}$	.0523
$m/10^{-24}g$	116
$(\eta_o/nm)/10^{-3}cm^2s^{-1}$	3.4
T_1/K	203
T_2/K	323

(3) For the incoherent scattering function $S_s(k;\omega)$ we used its hydrodynamic form which is known to represent a fairly good approximation up to k-values well beyond k_o, the main peak in the static structure factor $S(k)$. The diffusion constant is assumed to be of Arrhenius type $D(T)=D_o\exp(-T_o/T)$.

(4) In the approximation of the longitudinal and transverse current spectra $\Phi''_{L,T}(k;\omega)$ we used the fact that the vertex functions $W_{L,T}(k)$ which both are oscillating functions of k decreasing strongly for large k and vanishing quadratically for small k, have their main weight in different k-regions. While $W_L(k)$ is centered around k_o, $W_T(k)$ has its maximum values well below k_o. We therefore use $\Phi''_T(k;\omega)$ in its hydrodynamic form with the shear-viscosity of Arrhenius type /Ege 67/, $\eta(T)=\eta_o T/T_o \exp(T_o/T)$ and $\Phi''_L(k;\omega)\approx\pi S_s(k;\omega)\,\omega^2/\Omega_o^2(k)$ /Vin 58/ with $\Omega_o^2(k)=k_BT\,k^2/[mS(k)]$. Lacking more detailed information, $S(k)$ was taken from experiment at $T=T_2$ /BizB 77/ neglecting its temperature dependence. Since it is known that the main peak of $S(k)$ decreases with increasing temperature, we expect the decrease of $\tau_c(T)$ as a function of T (Fig. 2) to turn out somewhat less pronounced if actual $S(k)$ -values are inserted into eq. (5b) for higher temperatures.

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