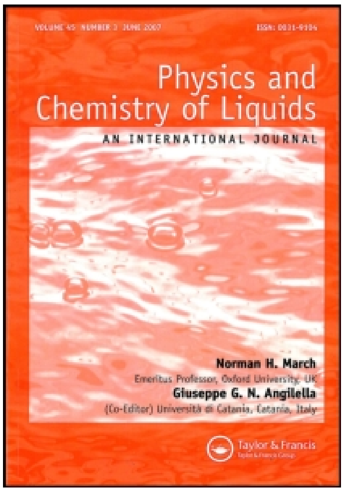

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T. Gaskell[a]
[a] Department of Physics, The University, Sheffield,

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Nuclear Quadrupolar Relaxation in Liquid Metals

T. GASKELL

Department of Physics, The University, Sheffield S3 7RH

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It is well known that the theory of the quadrupolar relaxation rate, R_{1Q}, may be expressed in liquids in terms of a time-dependent correlation function which describes the relative motion of the atoms. A new, intuitive approach to the correlation problem is developed, emphasising the effect of the close-range atomic encounters on the relaxation rate and an explicit $T^{-1/2}$ temperature dependence of the contribution to R_{1Q} from such processes is demonstrated. Other contributions are discussed, but since the experimental measurements of the quadrupolar relaxation rate in liquid metals indicate a close proportionality to $T^{-1/2}$ it is suggested that the short-range collisions play the dominant role in determining the relaxation rate.

1 INTRODUCTION

The interaction of the nuclear quadrupole moment and the fluctuating local electric field gradient arising from the thermal motion of the surrounding ions provides an important mechanism for spin-lattice relaxation in liquid metals and alloys. An expression for the quadrupolar relaxation rate, R_{1Q}, in a liquid metal in terms of a time-dependent correlation function was derived some years ago,[1] although some of the details have recently been revised.[2] However a common feature of both expressions is that they require for their evaluation a time-dependent correlation function which describes the relative motion of the ions in the liquid.

In a number of earlier theories it was concluded that the fluctuations in the electric field gradient resulted from single particle diffusion on a time scale which was characterized by the macroscopic self-diffusion coefficient D. This description has been criticized by Warren[3] on the grounds that the most significant contribution to the fluctuations will occur on a scale which reflects the motion of an ion over distances of the order of the interparticle separation. He derived an expression for R_{1Q} (also obtained independently by Sholl[4]) which contained the dynamic structure factor $S(q, \omega)$ as well as the self-correlation function, and argued that a major contribution to quadrupolar relaxation comes from low frequency modes with q values within a quite narrow range around the wavenumber at which the static structure factor has its principal peak.

The significant feature of the diffusion model is the prediction that $R_{1Q} \propto D^{-1}$ and that the temperature variation of R_{1Q} is therefore determined by the temperature dependence of the diffusion coefficient. In view of the lack of information about the temperature dependence of the dynamic structure factor, the predicted behaviour of R_{1Q} from the theory of Warren and Sholl is more difficult to establish. Sholl[4] concludes that R_{1Q} should decrease with increasing T but not quite as fast as D^{-1} dependence. Until more is known about the dynamic structure factor this conclusion must be regarded as somewhat tentative.

Experimental data on the quadrupolar relaxation rate follows a rather slower temperature variation than would be predicted by a D^{-1} dependence. In fact the experimental evidence indicates that R_{1Q} is closely proportional to $T^{-1/2}$ in a number of liquid metals.[5] The measurements on liquid gallium[6] and the more recent observations on liquid mercury,[7] amongst others, support this conclusion.

The purpose of this paper is to propose a rather different means of handling the time-dependent correlations and to examine, as far as possible, the consequences of this approach for the predicted temperature dependence of R_{1Q}. Now the magnitude of the electric field gradient decreases rapidly with increasing interatomic separation.[2] Because of this it seems clear that the rapid fluctuations in the gradients following the separation of two atoms after a direct collision will make a major, if not the most significant, contribution to the quadrupolar relaxation rate. On the basis of intuitive physical arguments we derive an expression which describes the effect of the short range encounters and discuss the temperature dependence of their contribution to R_{1Q}. We show that the contention that such processes dominate the fluctuations in the electric field gradients may be consistent with the $T^{-1/2}$ dependence of the relaxation rate which is observed experimentally. Unfortunately, the unknown temperature dependence of other quantities in our result precludes a firm prediction.

2 TIME-DEPENDENT CORRELATIONS

The Hamiltonian for a nuclear quadrupole moment interacting with an external electric field gradient may be expressed as

$$H_Q(t) = \sum_{m=-2}^{2} Q_m(I)F_{-m}(t) \tag{2.1}$$

$Q_m(I)$ is a quantity which depends upon the quadrupole moment, Q, and the nuclear spin operator I, and the $F_{-m}(t)$ are the electric field gradient components which transform as second-order spherical harmonics of index m. The fluctuations in the electric field components in a liquid contain frequencies which are much higher than the nuclear Larmor frequency ω_0 and as a consequence of this the nuclear magnetization relaxes exponentially to thermal equilibrium with a time constant T_1 which may be shown to be given by

$$T_1^{-1} = R_{1Q} = \frac{3(2I+3)(eQ)^2}{4I^2(2I-1)\hbar^2} J(0) \tag{2.2}$$

where

$$J(0) = J(m\omega_0) = \int_{-\infty}^{\infty} \mathrm{d}t \exp(-jm\omega_0 t)\langle F_m(t)F_{-m}(0)\rangle \tag{2.3}$$

with $m = 1$ or 2. The determination of R_{1Q}, therefore, reduces to the calculation of the time-dependent correlation functions $\langle F_m(t)F_{-m}(0)\rangle$ where the angular brackets denote a canonical ensemble average.

For a liquid containing N atoms in a volume V, the electric field gradient at a nucleus at the point $\mathbf{r}_0$, due to the other ions in the liquid, may be written in the form

$$F_m(t) = \sum_{i=1}^{N-1} U_m(\mathbf{r}_{i0}(t)) \tag{2.4}$$

with

$$U_m(\mathbf{r}_{i0}) = c\phi_2(r_{i0})(-1)^m Y_2^m(\Omega_{i0}) \cdot \quad c = (1-\gamma_\infty)\left(\frac{4\pi}{45}\right)^{1/2}$$

where γ_∞ is the Sternheimer antishielding factor and $\phi_2(r_{i0})$ is the radial part of the electric field gradient. It may be written in terms of a function $\phi(r)$ as

$$\phi_2(r) = \frac{\mathrm{d}^2\phi}{\mathrm{d}r^2} - \frac{1}{r}\frac{\mathrm{d}\phi}{\mathrm{d}r} \tag{2.5}$$

It has been pointed out by Schirmacher[2] that it is not strictly correct to take $\phi(r)$ to be the interatomic pair-potential, as had been assumed in earlier calculations.[4,8] He argues that the electric field gradient should be derived from the electric potential and not the potential energy, and he gives a prescription for calculating $\phi(r)$ in terms of an unscreened single-ion pseudopotential and the dielectric constant. However, an important point is that $\phi_2(r)$ whether evaluated from the potential, or using the prescription proposed by Schirmacher, decreases rapidly as r increases.

Now the ensemble average $\langle F_m(t)F_{-m}(0)\rangle$ is conveniently separated into two types of term. That is, we may write

$$\langle F_m(t)F_{-m}(0)\rangle = \left\langle \sum_{i=1}^{N-1} U_m(\mathbf{r}_{i0}(t))U_{-m}(\mathbf{r}_{i0}(0)) \right\rangle + \left\langle \sum_{i,j(i\neq j)} U(\mathbf{r}_{i0}(t))U_{-m}(\mathbf{r}_{j0}(0)) \right\rangle \tag{2.6}$$

The first expression on the right refers to correlations between the electric field gradient at the relaxing nucleus due to the same atom at two different times. The second between gradients at the relaxing nucleus from two different atoms. In the absence of any firm information about the three atom distribution function some form of superposition approximation is required even to obtain the initial value of the latter. It seems worth mentioning that an estimate of the magnitudes of the initial values of the two expressions can be important in assessing the relative importance of their contributions to the relaxation rate, a point which has perhaps not been emphasised sufficiently in the literature.

Consider the first term in (2.6)

$$\sum_{i=1}^{N-1} U_m(\mathbf{r}_{i0}(t))U_{-m}(\mathbf{r}_{i0}(0))$$

$$= \left\langle \sum_{i=1}^{N-1} \int \mathrm{d}\mathbf{y} U_m(\mathbf{r}_{i0}(0) + \mathbf{y})U_{-m}(\mathbf{r}_{i0})\delta(\mathbf{r}_{i0}(t) - \mathbf{r}_{i0}(0) - \mathbf{y}) \right\rangle \tag{2.7}$$

If we evaluate this expression in an approximate way by decoupling the ensemble average on the right hand side (2.7) becomes

$$\left\langle \sum_{i=1}^{N-1} U_m(\mathbf{r}_{i0}(t))U_{-m}(\mathbf{r}_{i0}(0)) \right\rangle$$

$$\simeq \left\langle \sum_{i=1}^{N-1} \int \mathrm{d}\mathbf{y}\, U_m(\mathbf{r}_{i0}(0) + \mathbf{y})U_{-m}(\mathbf{r}_{i0}(0)) \right\rangle \langle \delta(\mathbf{r}_{i0}(t) - \mathbf{r}_{i0}(0) - \mathbf{y})\rangle \tag{2.8}$$

$G(\mathbf{y}, t) \equiv \langle \delta(\mathbf{r}_{i0}(t) - \mathbf{r}_{i0}(0) - \mathbf{y})\rangle$ is a quantity which describes the relative motion of the two atoms, $\mathbf{y}$ being the change in separation during time t. The principal assumption in accepting the decoupling is that the motion of the atoms is independent of their initial configurations. This cannot be correct if the atoms are in close proximity and we shall subsequently modify our resulting expressions for the ensemble average in an intuitive way to compensate for this. The average over the initial positions in the first term on the right hand side of (2.8) is readily expressed through the radial distribution function, $g(r)$, so that

$$\left\langle \sum_{i=1}^{N-1} U_m(\mathbf{r}_{i0}(t))U_{-m}(\mathbf{r}_{i0}(0)) \right\rangle \simeq \rho \iint d\mathbf{r}\, d\mathbf{y}\, g(r)U_{-m}(\mathbf{r})U_m(\mathbf{r} + \mathbf{y})G(\mathbf{y}, t) \quad (2.9)$$

ρ being the number density.

In order to apply this result in a physically meaningful way to describe the close encounters we separate the field gradient into two parts. We make the separation at a value of $r = r_c$ where the interatomic potential may be conveniently divided into a strongly repulsive core and a softer long-ranged component. For example, we may define r_c as the value of r at which the interionic potential first falls to zero. When $r < r_c$ we refer to the field gradient as $U_m^c(\mathbf{r})$ and for $r \gtrsim r_c$ as $U_m^{lr}(\mathbf{r})$. We argue that those atoms whose cores are in contact at $t = 0$ will subsequently move apart under the mutual repulsion and we modify the latter equation to express this effect. The modification is such that for $t > 0$ the atoms will separate in a way that would be a consequence of a direct collision.[9] Hence

$$\begin{aligned} &\left\langle \sum_{i=1}^{N-1} U_m(\mathbf{r}_{i0}(t))U_{-m}(\mathbf{r}_{i0}(0)) \right\rangle \\ &\quad \simeq \rho \iint d\mathbf{r}\, d\mathbf{y}\, g(r)U_{-m}(\mathbf{r})U_m^c((r + y)\hat{\mathbf{r}})G(\mathbf{y}, t) \\ &\quad + \rho \iint d\mathbf{r}\, d\mathbf{y}\, g(r)U_{-m}(\mathbf{r})U_m^{lr}(\mathbf{r} + \mathbf{y})G(\mathbf{y}, t) \qquad (2.10) \end{aligned}$$

$G(\mathbf{y}, t)$ is essentially the probability density that the change in separation of two atoms in time t is $\mathbf{y}$. In the absence of a more satisfactory theory we shall approximate this by a self-correlation function but containing an effective mass $m^* = m/2$, the reduced mass in the relative motion of two atoms.[9] By making use of the Gaussian approximation for the self-correlation function, since it has proved to give a satisfactory description in liquids, and under the assumption that the atoms move independently after the collision we replace $G(\mathbf{y}, t)$ by $G_s^*(y, t)$ which is given by

$$G_s^*(y, t) = (4\pi a(t))^{-3/2} \exp\left(-\frac{y^2}{4a(t)}\right)$$

with

$$a(t) = \frac{k_B T}{m^*} \int_0^t ds(t - s)\psi(s)$$

and $\psi(s)$ the normalized velocity autocorrelation function. Note that for small values of y and t, $a(t)$ becomes $(k_B T/m)t^2$ and $G_s^*(y, t)$ then takes its ideal gas form. The angular integrations involving the spherical harmonics are trivially carried out for the core contribution in (2.10) and the equation reduces to

$$\left\langle \sum_{i=1}^{N-1} U_m(\mathbf{r}_{i0}(t))U_{-m}(\mathbf{r}_{i0}(0)) \right\rangle$$

$$\simeq 4\pi\rho c^2 \int_0^\infty \mathrm{d}r\, r^2 g(r)\phi_2^c(r) \int_0^\infty \mathrm{d}y\, y^2 \phi_2^c(r+y) G_s^*(y,t)$$

$$+ \rho \iint \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{y}\, g(r) U_m(\mathbf{r}) U_m^{lr}(\mathbf{r}+\mathbf{y}) G_s^*(y,t) \tag{2.11}$$

If we now turn our attention to the second term in Eq. (2.6), it soon becomes clear that the type of argument which has been used above is not easily justified in this case. Close proximity of the two atoms to the relaxing nucleus is not the only important condition to consider. The correlation between the two atoms themselves is crucial and their influence on the relaxing nucleus cannot be considered independently. Since the relative motion of more than two atoms is involved we shall use the well known space and time dependent distribution function, $G(\mathbf{r}, t)$, introduced by van Hove. This will be incorporated with a form of superposition approximation, which, as we suggested earlier is almost inevitable at the present time. The arguments are similar to those proposed by Warren and Sholl.[3,4] Now the three atom term in (2.6) is given by

$$\left\langle \sum_{i,j(i\neq j)} U_m(\mathbf{r}_{j0}(t))U_{-m}(\mathbf{r}_{i0}(0)) \right\rangle$$

$$= \iint \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{r}'\, U_m(\mathbf{r}')U_{-m}(\mathbf{r}) \left\langle \sum_{i,j(i\neq j)} \delta(\mathbf{r}' - \mathbf{r}_{j0}(t))\delta(\mathbf{r} - \mathbf{r}_{i0}(0)) \right\rangle \tag{2.12}$$

$\langle \sum_{i,j(i\neq j)} \delta(\mathbf{r} - \mathbf{r}_{i0}(0))\delta(\mathbf{r}' - \mathbf{r}_{j0}(t)) \rangle\, \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{r}'$ being essentially the joint probability of finding an atom within $\mathrm{d}\mathbf{r}$ at a distance $\mathbf{r}$ from the atom labelled 0 at $t = 0$, whilst at time t a different atom will be within the volume element $\mathrm{d}\mathbf{r}'$ at $\mathbf{r}'$ from 0. In Figure 1, $\mathbf{y}$ represents the migration distance of atom 0 in time t.

Now the probability of finding an atom, i, within $\mathrm{d}\mathbf{r}$ is $\rho g(r)\mathrm{d}\mathbf{r}$. Given that atom i is in the position shown, the probability that there will be another different atom j, at some later time t, a distance $\mathbf{y} + \mathbf{r}' + \mathbf{r}$ away within $\mathrm{d}\mathbf{r}'$ and that simultaneously atom 0 will migrate a distance $\mathbf{y}$ will be approximately represented by $G_d(|\mathbf{y} + \mathbf{r}' - \mathbf{r}|, t)G_s(y, t)$. $G_d(r, t)$ refers to the distinct part of the van Hove correlation function, $G(r, t)$, and is defined through the equation

$$G(r,t) = G_d(r,t) + G_s(r,t) \tag{2.13}$$

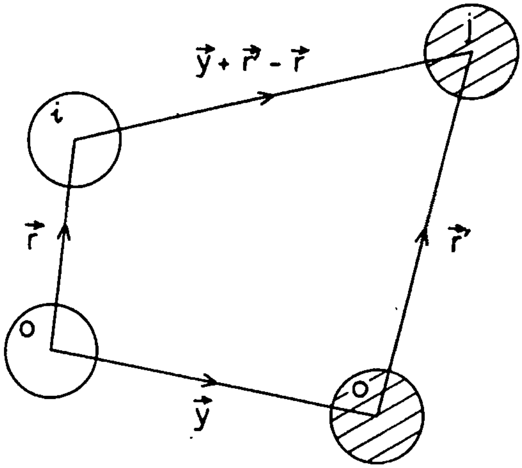

FIGURE 1 Open circles represent atomic positions at $t = 0$, and the hatched circles atomic positions at some later time t.

By decoupling the averages in this way we omit in the motion of the atoms subsequent to $t = 0$ the correlation in their final positions due to their mutual interaction and we attempt to correct this defect by multiplying the above result by $g(r_{j0}(t)) = g(r')$. The argument may be interpreted as a form of time-dependent superposition approximation. The joint probability is obtained by integrating over all possible values of y, and in this way

$$\left\langle \sum_{i,j(i\neq j)} \delta(\mathbf{r}-\mathbf{r}_{i0}(0))\delta(\mathbf{r}'-\mathbf{r}_{j0}(t)) \right\rangle d\mathbf{r}\, d\mathbf{r}' \simeq \rho g(r) g(r') \int G_d(|\mathbf{y}+\mathbf{r}'-\mathbf{r}|, t)\, G_s(y, t)\, d\mathbf{y}\, d\mathbf{r}\, d\mathbf{r}' \tag{2.14}$$

Hence the three atom term in (2.6) is expressed approximately as

$$\left\langle \sum_{i,j(i\neq j)} U_m(\mathbf{r}_{j0}(t))\, U_{-m}(\mathbf{r}_{i0}(0)) \right\rangle \simeq \rho \iint d\mathbf{r}\, d\mathbf{r}'\, g(r) g(r') U_m(\mathbf{r}') U_{-m}(\mathbf{r}) \int d\mathbf{y}\, G_d(|\mathbf{y}+\mathbf{r}'-\mathbf{r}|)\, G_s(y, t) \tag{2.15}$$

Introducing the quantities $F(k, t)$ and $F_s(k, t)$ through the equations

$$G_s(r, t) = \frac{1}{(2\pi)^3} \int d\mathbf{k}\, \exp(j\mathbf{k}\cdot\mathbf{r}) F_s(k, t)$$

$$G(r, t) = \rho + \frac{1}{(2\pi)^3} \int d\mathbf{k}\, \exp(j\mathbf{k}\cdot\mathbf{r}) F(k, t)$$

we have

$$G_d(r, t) = \rho + \frac{1}{(2\pi)^3} \int d\mathbf{k} \exp(j\mathbf{k} \cdot \mathbf{r})[F(k, t) - F_s(k, t)]$$

When these expressions are used in (2.15) the constant density term does not contribute because of the independent angular integrations over the spherical harmonics and consequently the equation becomes

$$\left\langle \sum_{i, j(i \neq j)} U_m(\mathbf{r}_{j0}(t)) U_{-m}(\mathbf{r}_{i0}(0)) \right\rangle$$

$$\simeq \frac{\rho}{(2\pi)^3} \iint d\mathbf{r}\, d\mathbf{r}'\, g(r) g(r') U_m(\mathbf{r}') U_{-m}(\mathbf{r}) \int d\mathbf{k} \exp(j\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}'))$$

$$\times [F(k, t) - F_s(k, t)] F_s(k, t) \tag{2.16}$$

The initial value of the right hand side agrees with that obtained by using the Born–Green–Kirkwood superposition approximation. By means of the standard expansion for each of the plane wave components in (2.16), namely

$$\exp(j\mathbf{k} \cdot \mathbf{r}) = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} j^l j_l(kr) Y_l^m(\theta_k, \phi_k) Y_l^{m*}(\theta_r, \phi_r)$$

where $j_l(kr)$ is a spherical Bessel's function of order l, the above equation, after carrying out the angular integrations, may be further reduced to

$$\left\langle \sum_{i, j(i \neq j)} U_m(\mathbf{r}_{j0}(t)) U_{-m}(\mathbf{r}_{i0}(0)) \right\rangle$$

$$\simeq \frac{\rho c^2}{(2\pi)^3} \int_0^\infty dk \left(4\pi \int_0^\infty dr\, r^2 g(r) \phi_2(r) j_2(kr) \right)^2 k^2 [F(k, t) - F_s(k, t)] F_s(k, t) \tag{2.17}$$

where the spherical Bessel's function is given by

$$j_2(x) = x^{-3}[(3 - x^2)\sin x - 3x \cos x]$$

Similar techniques may be used to handle the angular integrations involved in the long-ranged component in Eq. (2.11).

Collecting the terms in (2.11) and (2.17) the autocorrelation function of the field gradient is approximately represented in the following way

$$\langle F_m(t)F_{-m}(0)\rangle = 4\pi\rho c^2 \int_0^\infty \mathrm{d}r\, r^2 g(r)\phi_2^c(r) \int_0^\infty \mathrm{d}y\, y^2 \phi_2^c(r+y) G_s^*(y,t)$$
$$+ \frac{\rho c^2}{(2\pi)^3} \int_0^\infty \mathrm{d}k \left[4\pi \int_0^\infty \mathrm{d}r\, r^2 g(r)\phi_2(r) j_2(kr) 4\pi \int_0^\infty \mathrm{d}s\, s^2 \phi_2^{lr}(s) j_2(ks) \right] k^2 F_s^*(k,t)$$
$$+ \frac{\rho c^2}{(2\pi)^3} \int_0^\infty \mathrm{d}k \left(4\pi \int_0^\infty \mathrm{d}r\, r^2 g(r)\phi_2(r) j_2(kr) \right)^2 k^2 [F(k,t) - F_s(k,t)] F_s(k,t) \tag{2.18}$$

the right hand side being independent of subscript m.

In the theories of Warren and Sholl[3,4] the two and three particle terms in the autocorrelation function are not considered independently. Instead a joint probability function is derived which contains the van Hove correlation function $G(r, t)$ in an attempt to describe both types of term in a single expression. If the contributions to our result in (2.18), whose time dependence is determined solely by the self-correlation function, cancelled exactly we would recover the result of Warren and Sholl. In general such a cancellation would be fortuitous. Our approach explicitly emphasises the influence of the short range collisions and it is the temperature dependence of their contribution to R_{1Q} with which we shall be mainly concerned.

3 TEMPERATURE DEPENDENCE OF THE QUADRUPOLAR RELAXATION RATE

We shall introduce a function $R(t)$, defined by the equation

$$R(t) = \lambda \langle F_m(t)F_{-m}(0)\rangle \tag{3.1}$$

where

$$\lambda = \frac{3(2I+3)(eQ)^2}{4I^2(2I-1)\hbar^2}$$

and from Eq. (2.2) it follows that the relaxation rate

$$R_{1Q} = \int_{-\infty}^{\infty} R(t)\mathrm{d}t$$

Without detailed knowledge of several quantities in the expression for the autocorrelation function a firm prediction of the temperature dependence of R_{1Q} is difficult. However, it is possible to make some comments about the temperature dependence arising from the close encounters expressed in the first term in (2.18). Because of the way in which we have defined $\phi_2^c(r)$ and the form of the radial distribution function for $r \lesssim r_c$, it is clear that only small values of y will contribute to the integral. Although the time integration of the modified self-correlation function, $G_s^*(y, t)$, is not generally known we may *justifiably* use the ideal gas form in this limit. For this situation it follows that

$$\int_{-\infty}^{\infty} dt\ G_s^*(y, t) \to \frac{1}{\pi}\left(\frac{m^*}{2\pi k_B T}\right)^{1/2}\frac{1}{y^2}$$

If we denote the two and three particle contributions to $R(t)$ by $R_{(2)}(t)$ and $R_{(3)}(t)$ respectively, then form (2.18), on carrying out the y integration we obtain

$$\int_{-\infty}^{\infty} R_{(2)}^c(t)dt = 4\rho c^2\lambda\left(\frac{m^*}{2\pi k_B T}\right)^{1/2}\int_0^{r_c} dr\ r^2 g(r)\phi_2^c(r)\left[-\frac{d\phi^c}{dr}(r) + \frac{1}{r}\phi^c(r)\right] \tag{3.2}$$

The second term within the bracket has only been integrated approximately, but the error should not be significant since we expect the first term to be much the more important.

In Sholl's (1974) paper, where $\phi_2(r)$ was evaluated using the pair-potential, it was demonstrated that the characteristic features of $g(r)$ and $\phi_2(r)$ where such that the product of the two was a sharply peaked function at a value of r close to the core diameter. This has yet to be confirmed when $\phi_2(r)$ is obtained in the way suggested by Schirmacher,[2] but if we speculate that this remains the case it would mean that the long-ranged component of $\phi_2(r)$ is not very significant. The contribution of the two particle terms may then effectively be reduced to a single expression since the close collisions would dominate. It would take the form of (3.2) and could be further simplified in the following way. If the major contribution to the product $r^2g(r)\phi_2(r)$ arises from a narrow region in r space around the atomic core diameter, r_c, we approximate the latter by a delta function at $r = r_c$. We therefore introduce the equation

$$\frac{4\pi\rho}{3m} r^2 g(r)\phi_2(r) \simeq \bar{w}^2\delta(r - r_c) \tag{3.3}$$

where

$$\bar{\omega}^2 = \frac{4\pi\rho}{3m}\int_0^{\infty} dr\ r^2 g(r)\phi_2(r)$$

If $\phi(r)$, in the definition of $\phi_2(r)$ given in (2.5), closely resembles the interionic potential then the second derivative of $\phi(r)$ will dominate the integrand so that ϖ is of the order of the maximum phonon frequency in the solid. Hence

$$\int_{-\infty}^{\infty} R_{(2)}(t)\mathrm{d}t = 3mc^2\lambda\frac{1}{\pi}\left(\frac{m^*}{2\pi k_B T}\right)^{1/2}\varpi^2\left[-\frac{\mathrm{d}\phi}{\mathrm{d}r}(r_c) + \frac{1}{r_c}\phi(r_c)\right] \quad (3.4)$$

There is an explicit $T^{-1/2}$ temperature dependence therefore in that part of the relaxation rate which arises from close encounters between two atoms. However, if the experiments which determine the temperature variation of the relaxation rate were carried out at constant density, it seems reasonable to suppose that the integrated product $r^2 g(r)\phi_2(r)$ will increase as the temperature is increased. This is because $g(r)$ will move inwards under these conditions where $\mathrm{d}^2\phi/\mathrm{d}r^2$ increases more rapidly, and will be particularly marked if Eq. (3.3) represents a good approximation. This effect may be nullfied to some extent by a broadening of the principal peak of $g(r)$. Hence one anticipates a slower decrease than $T^{-1/2}$. It should be pointed out, however, that the experiments are not carried out along an isochore so that the above argument is not strictly applicable to the existing experimental results.

The same type of uncertainty will be involved in assessing the contribution of the three particle terms in Eq. (2.18). Nevertheless we can say that because $F(k, t) \rightarrow F_s(k, t)$ for large values of k there will be no significant contribution to $R_{(3)}(t)$ in this limit. In other words the effect of close collisions, which produce large momentum transfers, is not important here. However, cooperative modes of motion, involving small and intermediate range wavenumbers may play an important role. It is possible to reduce the expression if we are prepared to make certain simplifying assumptions about the time dependence of the functions $F_s(k, t)$ and $F(k, t)$. Their Fourier transforms are generally denoted by $S_s(k, w)$ and $S(k, w)$ respectively, the latter being the dynamic structure factor of the liquid. It has been suggested that both $S_s(k, w)$ and $S(k, w)$ may reasonably be supposed to have Lorentzian frequency distributions of equal width centred at the origin.[3,8] If this is so it is easily shown that

$$\int_{-\infty}^{\infty} R_{(3)}(t)\mathrm{d}t = \frac{\rho c^2\lambda}{8\pi^2}\int_0^{\infty}\mathrm{d}k\left(4\pi\int_0^{\infty}\mathrm{d}r\, r^2 g(r)\phi_2(r)j_2(kr)\right)^2 k^2[S(k,0) - S_s(k,0)] \quad (3.5)$$

If we speculate that the approximation suggested in (3.3) is valid, then this result simplifies to

$$\int_{-\infty}^{\infty} R_{(3)}(t)\mathrm{d}t = \frac{9m^2c^2\lambda}{8\pi^2\rho}\,\varpi^4\int_0^{\infty}\mathrm{d}k\, j_2^2(kr_c)k^2[S(k,0) - S_s(k,0)] \quad (3.6)$$

No convincing theory of the dynamic structure factor in the quasi-elastic region around $S(k, 0)$ is available, although there are a number of approximation which attempt to relate $S(k, \omega)$ to its self part $S_s(k, \omega)$. A summary of the details has been given by Schirmacher.[10] The Lorentzian form for $S_s(k, \omega)$ is certainly true when the time scale is such that the single particle motion is characterized by the macroscopic diffusion coefficient. In this case $S_s(k, 0) = (\pi Dk^2)^{-1}$ and on the basis of the above approximation it would appear that the temperature dependence is largely determined by that of the diffusion coefficient. However, it is difficult to justify the use of the hydrodynamic form for $S_s(k, 0)$ because it appears from Warren's calculations[3] that the range of wavenumbers which lie around the principal peak in the structure factor can be very important. Unlike the two particle terms therefore it will be difficult to determine the temperature dependence of the above equations without detailed numerical calculation. It should perhaps be emphasised again that some significant temperature dependence may arise through the factor $\bar{\omega}^4$ in (3.6), particularly along an isochore.

4 DISCUSSION

We have described the effects of the short-range encounters on the quadrupolar relaxation rate and for such contributions have demonstrated an explicit $T^{-1/2}$ dependence. An assumption that such processes dominate the relaxation rate would seem to be consistent with the experimentally observed temperature dependence for a number of liquid metals. This would imply that the contribution from the long-range component of the field gradient and that from the three particle terms are either small or show a marked degree of cancellation. When reliable results for the field gradient become available this can be properly investigated. At the present time only some preliminary attempts to calculate the latter have been made.[11]

Our result for the relaxation rate contains products of the radial part of the electric field gradient between two ions and the radial distribution function arising from the ensemble averages involved. If the characteristic features of these two functions are such that the major contribution arises from the region around the core diameter one might anticipate a significant temperature dependent contribution to arise from such terms. This is because two ions will be capable of closer approach as the temperature is raised and the field gradient increases rapidly as the separation decreases. The effect will be most marked if the density remains constant, where we would predict a slower temperature variation than $T^{-1/2}$. No such experiments appear to have been undertaken as yet.

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