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Nuclear quadrupolar relaxation in monatomic liquids

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A general theory is described for nuclear quadrupolar spin-lattice relaxation in monatomic liquids. The theory is valid for either liquid rare gases or liquid metals when appropriate forms are taken for the local electric field gradient (EFG). It is shown that the relaxation rate may be approximated in terms of an integral over the "elastic" limit $S(k, 0)$ of the dynamic liquid structure factor multiplied by a weighting factor $I(k)$ determined by the spatial variation of the EFG. Calculations of $I(k)$ for Ne and Ga identify the ranges of k values responsible for quadrupolar relaxation in these liquids. For Ne, the dominant modes fall in the range $K_0 \lesssim k \lesssim 2K_0$, where K_0 is the position of the main peak in the static liquid structure factor. For Ga, and for metals in general, $I(k)$ is largest near twice the Fermi wave vector ($2k_F$) if the EFG is determined from the asymptotic form of a screened ionic potential. For both liquid rare gases and liquid metals, these relatively high k values indicate that collective motions play an important role in the nuclear relaxation process. As a corollary it is shown that magnetic dipolar relaxation in monatomic liquids can be described as a special case of the general theory with appropriate changes of the coupling constants. Numerical calculations of the relaxation rate for Ne^{21} and Ga^{69} near their respective melting points and the temperature dependence of the Ne^{21} rate are in good agreement with experiment.

I. INTRODUCTION

Nuclear electric quadrupolar interactions provide an important mechanism for spin-lattice relaxation in monatomic liquids. In liquid rare gases, for example, quadrupolar relaxation has been found to dominate the spin-lattice relaxation of nuclei with spin greater than $\frac{1}{2}$.[1-3] In elemental liquid metals the quadrupolar process competes on roughly equal terms with magnetic dipolar relaxation via couplings to the conduction-electron spins. Quadrupolar relaxation can be directly measured in a few liquid metals for which measurements on two isotopic species permit experimental separation of magnetic and quadrupolar contributions.[4-7] In a number of others, the presence of quadrupolar relaxation has been inferred by means of theoretical estimates of the magnetic contribution.[5,6,8-11]

Nuclear quadrupolar relaxation results from the interaction between the nuclear electric quadrupole moment and the local electric field gradient (EFG) associated with the nuclear environment. Motions of neighboring electronic and nuclear charge distributions cause the EFG to vary in time and the resulting time-dependent interaction induces transitions between nuclear Zeeman levels, i.e., spin-lattice relaxation.[12] The strength and temperature dependence of the relaxation process are therefore governed by the dynamics of the local charge distribution.

In liquid rare gases the local EFG results from distortion of the closed shell atomic configuration by neighboring atoms. The time dependence of the quadrupolar interaction therefore is determined by the relative thermal motions of atoms. In liquid metals, the situation is slightly more complex since both conduction electron and ionic charges must be considered and these have different motional properties. There are two types of quadrupolar relaxation possible in metals. In one process, the time-dependent EFG results from translational motion of the charge of electrons having p or d character at the nucleus.[13,14] Relaxation results from a scattering process analogous to the well-known Korringa magnetic process.[15] The second process results from the motion of ions whose screened charge produces EFGs at neighboring nuclei.[8,9,16-18] Estimates of the strength of the electronic scattering process have shown it to be too weak to account for the observed quadrupolar relaxation in liquid metals.[5,13,14] Although the EFG associated with the screened ion is of the same order of magnitude as that of the electronic charge, the slower ionic movements produce a perturbation in better tune with the nuclear frequency ($\omega_0 \sim 10^8$ Hz). It is therefore most likely that ionic motions are responsible for quadrupolar relaxation in liquid metals just as atomic motions play this role in liquid rare gases.

A number of theories have been advanced in order to explain quadrupolar relaxation, specifically in the context of liquid metals.[9,16-18] These theories differ in the sophistication of their approaches, but in each case it is assumed that the EFG fluctuations result from translational single-particle diffusion. Furthermore, it has been universally assumed that the translational motion can be characterized by the macroscopic self-diffusion coefficient D. This description ought to be questioned on the grounds that the most important motions occur on the scale of the interparticle distance, whereas the coefficient D characterizes the average motion of a particle over macroscopic distances. On the microscopic scale, it is necessary to consider not only simple translational motions but also the possibility of short wavelength vibrational modes and collective or correlated motions of several particles.

In addition to the above intuitive arguments there is ample experimental evidence that macroscopic diffusion does not provide an adequate description of nuclear quadrupolar relaxation. The diffusion model predicts that the temperature dependence of the quadrupolar relaxation rate is described approximately by

$$R_Q \propto \rho D^{-1}, \tag{1}$$

where ρ is the density.[9,16] Since both ρ and D^{-1} decrease with temperature, Eq. (1) predicts that R_Q should decrease with increasing temperature. However, this behavior has never been observed experimentally. The observed relaxation rates always decrease less rapidly than ρD^{-1} and, in some liquid metals, R_Q may become temperature independent,[7] or even increase with temperature.[5] In a theory developed by Sholl,[17] the most detailed diffusional theory to appear so far, there is an additional temperature-dependent factor:

$$R_Q \propto \rho D^{-1}(I_1 + 2\pi\rho I_2), \tag{2}$$

where I_1 and I_2 are integrals involving the EFG and the (temperature-dependent) pair distribution function $g(r)$. A tendency for I_1 and I_2 to increase with temperature would weaken the variation of R_Q relative to Eq. (1), but it is unlikely that this effect is large enough to explain the experimental discrepancies. A further difficulty with Eq. (2) is that I_1 and $2\pi\rho I_2$ have opposite signs and comparable magnitudes so that I_1 and I_2 must be known with great precision in order to accurately predict the behavior of R_Q.

This paper will describe a new and more general theory of nuclear quadrupolar relaxation in monatomic liquids. With the help of certain simplifying assumptions the relaxation rate will be expressed in a form such that the important microscopic motions may be identified more clearly than previously possible. Specifically, the rate R_Q will be expressed in terms of the low frequency limit of the dynamic structure factor $S(k, \omega)$. This function contains the basic information about single-particle and two-particle correlated motions and has been extensively studied both theoretically, and experimentally by scattering light and thermal neutrons. The formulation to be described, while approximate, permits the incorporation of knowledge of the liquid dynamics obtained by other techniques and, hopefully, may extend the usefulness of quadrupolar relaxation as a probe of dynamic liquid structure.

The organization of this paper is as follows. In Sec. II the general theory is described and a simple integral relation between $S(k, 0)$ and R_Q is presented. Sections III and IV describe, respectively, specific forms for the EFG and $S(k, 0)$ for both liquid rare gases and liquid metals. In Sec. V numerical results are presented for two illustrative cases—liquid Ne and Ga—and compared with the diffusion model and with experiment. Finally, in Sec. VI, the work is summarized and the main conclusions are presented.

II. THEORY

A. Electric quadrupolar relaxation rate

The nuclear electric quadrupolar interaction may be conveniently expressed in terms of nuclear functions Q^m and EFG components $V^m(t)$ which transform as second-order spherical harmonics of index m[12]:

$$\mathcal{H}_Q(t) = \sum_{m=-2}^{2} Q^m V^{-m}(t). \tag{3}$$

The nuclear functions Q^m depend on the nuclear quadrupole moment Q and components of the nuclear spin operator $\vec{I}$:

$$Q^0 = A[3I_z^2 - I(I+1)], \tag{4a}$$

$$Q^{\pm 1} = \sqrt{\tfrac{3}{2}}\, A(I_z I_\pm + I_\pm I_z), \tag{4b}$$

$$Q^{\pm 2} = \sqrt{\tfrac{3}{2}}\, A I_\pm^2, \tag{4c}$$

where $I_\pm = I_x \pm i I_y$ and $A = eQ/2I(2I-1)$. The EFG components depend on the second derivatives of the total time-dependent potential at the nucleus $V(t)$:

$$V^0(t) = \tfrac{1}{2}[V_{zz}(t) - \tfrac{1}{3}\nabla^2 V(t)], \tag{5a}$$

$$V^{\pm 1}(t) = (1/\sqrt{6})[V_{xz}(t) \pm i V_{yz}(t)], \tag{5b}$$

$$V^{\pm 2}(t) = (1/2\sqrt{6})[V_{xx}(t) - V_{yy}(t) \pm 2i V_{xy}(t)]. \tag{5c}$$

In Eqs. (4) and (5) components of the spin-operators and EFG are taken in the laboratory coordinate system and the magnetic field has been assumed to lie along the z direction.

In liquids, fluctuations of the EFG components $V^m(t)$ contain frequency components much higher than the nuclear Larmor frequency ω_0. In this so-called "extreme narrowing" limit, it can be shown from first-order time-dependent perturbation theory that the nuclear magnetization relaxes to thermal equilibrium according to a single exponential behavior with time constant T_1:

$$T_1^{-1} \equiv R_Q = \tfrac{3}{4} f(I)(eQ/\hbar)^2 J(0), \tag{6}$$

where $f(I) = (2I+3)/I^2(2I-1)$.[19] The spectral functions $J(0) = J_1(\omega_0) = J_2(2\omega_0)$ are given by

$$J_1(\omega_0) = \int_{-\infty}^{\infty} e^{-i\omega_0 t} \langle V^1(t) V^{-1}(0)\rangle_{\text{av}}\, dt, \tag{7a}$$

$$J_2(2\omega_0) = \int_{-\infty}^{\infty} e^{-2i\omega_0 t} \langle V^2(t) V^{-2}(0)\rangle_{\text{av}}\, dt, \tag{7b}$$

and the $\langle\ \rangle_{\text{av}}$ denote ensemble averages. Since all factors in Eq. (6) are known except $J(0)$, the problem reduces to calculation of the time-dependent correlation functions $\langle V^m(t) V^{-m}(0)\rangle_{\text{av}}$.

We suppose that the potential V at some nucleus of interest can be represented as a sum of contributions v_i which depend on the relative displacement $\vec{r}_i$ of the ith neighboring atom. If there are N atoms in the system, we have for each EFG component

$$V^m(t) = \sum_{i=1}^{N-1} v^m[\vec{r}_i(t)]. \tag{8}$$

Then, with the help of Eq. (8), the ensemble averages in Eqs. (7a) and (7b) may be expressed in terms of an integral over a probability function $P(\vec{r}_0, 0; \vec{r}_1, t)$,

$$\langle V^m(t) V^{-m}(0)\rangle_{\text{av}} = \int\int d\vec{r}_0\, d\vec{r}_1\, v^m(\vec{r}_1) v^{-m}(\vec{r}_0) \times P(\vec{r}_0, 0; \vec{r}_1, t), \tag{9}$$

where P is the joint probability that when $t=0$ an atom is located at $\vec{r}_0$ relative to the atom of interest and at time t there is an atom at relative position $\vec{r}_1$. Since the atom at $\vec{r}_1$ may or may not be the same as the one initially located at $\vec{r}_0$, the joint probability function P involves both two- and three-particle correlations in the liquid.

B. Joint probability function

It is clear from Eq. (9) that the essence of the theory of quadrupolar relaxation in liquids resides in the joint probability function $P(\vec{r}_0, 0; \vec{r}_1, t)$ through which the dynamic liquid structure influences the relaxation rate. The present theory is based on a simple expression of $P(\vec{r}_0, 0; \vec{r}_1, t)$ in terms of the van Hove time-dependent pair distribution function $G(\vec{r}, t)$,[20] and the static pair distribution function $g(r)$. Recall that $g(r)$ is the average probability that an atom will be located a distance r from the atom of interest. $G(\vec{r}, t)$ is the probability that if an atom is located initially at the origin, an atom (not necessarily the same one) will be found at a later time t at point $\vec{r}$ relative to the initial fixed origin. It is evident that any expression of $P(\vec{r}_0, 0; \vec{r}, t)$ in terms of $G(\vec{r}, t)$ must be approximate since the former includes three-body correlations while $G(\vec{r}, t)$ is, by definition, a two-body correlation function.

To form the joint probability function consider the initial and final configurations of atoms illustrated in Fig. 1. The probability of the initial configuration is simply $\rho g(r_0)$. Now let us assume that the correlation of the atom (i) at relative position $\vec{r}_0$ and the atom (j) at relative position $\vec{r}_1$ is *independent* of the motion of the atom of interest, except that the final positions of the atom of interest and atom (j) must be correlated by the average pair distribution $g(r_1)$. Then since the correlation of atoms (i) and (j) is described by $G(\vec{r}+\vec{r}_1-\vec{r}_0, t)$ and the motion of the atom of interest is described by the "self" part of the van Hove function $G_s(\vec{r}, t)$, the joint probability with a given displacement $\vec{r}$ of the atom of interest is $\rho g(r_0) G(\vec{r}+\vec{r}_1-\vec{r}_0, t) \times G_s(\vec{r}, t) g(r_1)$. The total joint probability is then obtained by integrating over all values of $\vec{r}$:

$$P(\vec{r}_0, 0; \vec{r}_1, t) = \rho g(r_0) g(r_1) \times \int d\vec{r}\, G_s(\vec{r}, t)\, G(\vec{r}+\vec{r}_1-\vec{r}_0, t). \tag{10}$$

It should be emphasized that Eq. (10) is not exact but has been constructed by means of simple physical assumptions. The validity of this form will be considered shortly by examination of its limiting

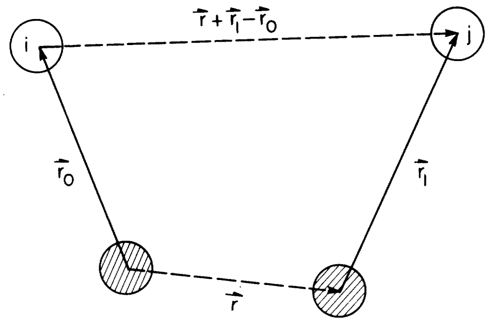

FIG. 1. Derivation of the joint probability function $P(\vec{r}_0, 0; \vec{r}_1, t)$. The probability of the initial configuration $\rho g(r_0)$ is multiplied by the conditional probability $G_s(\vec{r}, t) G(\vec{r}+\vec{r}_1-\vec{r}_0, t) g(r_1)$ that an atom will be located at $\vec{r}_1$ relative to the atom of interest (shaded) given the initial configuration. The atom (j) at relative position $\vec{r}_1$ at time t is not necessarily the same as the atom (i) initially at $\vec{r}_0$. It is assumed that the self-motion of the atom of interest over the distance $\vec{r}$ is independent of the correlation of atoms (i) and (j). The total probability function of Eq. (10) is obtained by integrating over all possible displacements $\vec{r}$ of the atom of interest.

behavior.

The integral in Eq. (10) may be approximated using an additional assumption. It is convenient to first introduce the dynamic structure factors $S_s(k,\omega)$ and $S(k,\omega)$ which are related to $G_s(\vec{r},t)$ and $G(\vec{r},t)$ by Fourier transforms:

$$G_s(\vec{r},t)=(1/2\pi)^3\int\int d\vec{k}\,d\omega\,e^{-(\vec{k}\cdot\vec{r}-\omega t)}S_s(k,\omega),\tag{11a}$$

$$G(\vec{r},t)=\rho+(1/2\pi)^3\int\int d\vec{k}\,d\omega\,e^{-i(\vec{k}\cdot\vec{r}-\omega t)}S(k,\omega).\tag{11b}$$

Substitution of Eqs. (11a) and (11b) into the integral in Eq. (10) and integration over $\vec{r}$ yields

$$\begin{aligned}\int d\vec{r}\,G_s(\vec{r},t)\,G(\vec{r}+\vec{r}_1-\vec{r}_0,t)&\\ =\rho+(1/2\pi)^3\int d\vec{k}\,e^{-i[\vec{k}\cdot(\vec{r}_1-\vec{r}_0)]}&\\ \times\int\int d\omega\,d\omega'\,e^{i(\omega+\omega')t}S(k,\omega)S_s(k_s\omega').&\end{aligned}\tag{12}$$

Let us now assume (to be justified shortly) that $S(k,\omega)$ and $S_s(k,\omega)$ are Lorentzian functions of ω having the same widths. Then since $S_s(k,\omega)$ is normalized to unity,

$$\int d\omega'\,S_s(k,\omega')=1,\tag{13}$$

it is easy to show that

$$\int\int d\omega\,d\omega\,e^{i(\omega+\omega')t}S(k,\omega)S_s(k,\omega')\rightarrow\int d\omega\,e^{i2\omega t}S(k,\omega).\tag{14}$$

Then substituting the approximation given by Eq. (14) into Eq. (12) and comparing with Eq. (11b) we find

$$\int d\vec{r}\,G_s(\vec{r},t)\,G(\vec{r}+\vec{r}_1-\vec{r}_0,t)\rightarrow G(\vec{r}_1-\vec{r}_0,2t),\tag{15}$$

and, finally, from Eq. (10),

$$P(\vec{r}_0,0;\vec{r}_1,t)=\rho g(r_0)g(r_1)G(\vec{r}_1-\vec{r}_0,2t).\tag{16}$$

Before proceeding further let us review the assumptions invoked in the derivation of Eq. (16). The first of these is the assumption of independent motion of the atom of interest used to formulate Eq. (10). This expression of three-particle correlations in terms of two-particle correlation functions is a kind of dynamic analogue of the Kirkwood superposition approximation for the static three-particle distribution function.[21] Indeed in the limit $t\rightarrow 0$, $G(\vec{r},t)\rightarrow\delta(\vec{r})+\rho g(r)$, and from Eq. (16),

$$\begin{aligned}&P(\vec{r}_0,0;\vec{r}_1,0)\\ &\quad=\rho g(r_0)g(r_1)\delta(\vec{r}_1-\vec{r}_0)+\rho^2g(r_0)g(r_1)g(|\vec{r}_1-\vec{r}_0|).\end{aligned}\tag{17a}$$

This may be compared with the exact limit

$$P(\vec{r}_0,0;\vec{r}_1,0)=\rho g(r_0)\delta(\vec{r}_1-\vec{r}_0)+\rho^2g^3(\vec{r}_0,\vec{r}_1),\tag{17b}$$

where $g^3(\vec{r}_0,\vec{r}_1)$ is the three-particle distribution function. The second term on the right-hand side of Eq. (17a) is just the Kirkwood approximation for $g^3(\vec{r}_0,\vec{r}_1)$. The first terms of Eqs. (17a) and (17b) differ by a factor $g(r_1)$. This discrepancy could be eliminated if, in the construction of Eq. (10), the factor $[g(r_1)/g(r_0)]^{1/2}$ had been used to correlate the final positions of the particles, rather than $g(r_1)$. However, this would destroy the correspondence with the Kirkwood approximation. It can be estimated from Eq. (9) that use of Eq. (17a) leads to less than 10% error in the magnitude of the correlation functions at $t=0$. At very long times $G(\vec{r}_1-\vec{r}_0,2t)\rightarrow\rho$ and

$$P(\vec{r}_0,0;\vec{r}_1,\infty)=\rho^2g(r_0)g(r_1),\tag{18}$$

which simply states that the initial and final configurations become uncorrelated as $t\rightarrow\infty$. Thus, Eq. (16) represents a reasonably accurate approximation at short times and becomes rigorously correct at long times.

The assumption that $S_s(k,\omega)$ and $S(k,\omega)$ are Lorentzians of equal widths, has some experimental basis. Sköld *et al.* recently compared careful measurements of $S(k,\omega)$ and $S_s(k,\omega)$ for liquid Ar.[22] They found that both were closely Lorentzian except in the high frequency wings. We know *a priori* that widths of the two functions cannot be greatly different since both must have the same second moment,

$$\int d\omega\,\omega^2S_s(k,\omega)=\int d\omega\,\omega^2S(k,\omega)=(k_BT/M)k^2,\tag{19}$$

where T is the absolute temperature and M is the atomic mass. In fact, the widths at half-maximum were found to differ by roughly (20–30)% in the range of k values near the maximum in the structure factor which (as we shall show) is most important for quadrupolar relaxation. It is easy to include such a correction to Eq. (14) and subsequent development. However, it turns out that a width difference of 30% between $S(k,\omega)$ and $S_s(k,\omega)$ alters the final result for R_Q by only about 2%. Since this is smaller than other uncertainties that come into actual calculations, the approximation of Eq. (14) will be assumed in the interest of simplicity. A more precise formulation is outlined in Appendix A, where the condition of equal widths is relaxed.

C. Spectral density functions

The final step in calculating the relaxation rate is evaluation of the spectral density function $J(0)$ in Eq. (6). Substituting Eq. (16) for $P(\vec{r}_0, 0; \vec{r}_1, t)$ into Eq. (9), we have from Eqs. (7a) and (7b)

$$J_m(m\omega_0) = \rho \int\int d\vec{r}_0 d\vec{r}_1 v^m(\vec{r}_1) v^{-m}(\vec{r}_0) g(r_0) g(r_1) \times \int_{-\infty}^{\infty} dt\, e^{-im\omega_0 t} G(\vec{r}_1 - \vec{r}_0, 2t). \tag{20}$$

Replacing $G(\vec{r}_1 - \vec{r}_0, 2t)$ by its Fourier transform, Eq. (11b), and integrating over t we find

$$J_m(m\omega_0) = (\rho/8\pi^2) \int d\vec{k} S(k, \tfrac{1}{2}m\omega_0) \times \int\int d\vec{r}_0 d\vec{r}_1 v^m(\vec{r}_1) v^{-m}(\vec{r}_0) \times g(r_0) g(r_1) e^{-i\vec{k}\cdot(\vec{r}_1 - \vec{r}_0)}. \tag{21}$$

Now for a central potential $v(r)$, the EFG functions have the following important property:

$$v^{\pm m}(\vec{r}) = \left(\frac{4\pi}{45}\right)^{1/2} r \frac{d}{dr}\left(\frac{1}{r}\frac{dv}{dr}\right)(\mp 1)^m Y_2^{\pm m}(\theta_r, \varphi_r) \equiv F(r)(\mp 1)^m Y_2^{\pm m}(\theta_r, \varphi_r), \tag{22}$$

where $F(r)$ determines the radial dependence of the EFG and $Y_2^m(\theta_r, \varphi_r)$ is the normalized second-order spherical harmonic of the atomic angular coordinates. The exponential in Eq. (21) may also be expressed in terms of spherical harmonics using the standard expansion

$$e^{i\vec{k}\cdot\vec{r}} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^l j_l(kr) Y_l^{m*}(\theta_k, \varphi_k) Y_l^m(\theta_r, \varphi_r), \tag{23}$$

where $j_l(kr)$ is a spherical Bessel function of order l. Then Eqs. (22) and (23) may be substituted into Eq. (21), and the angular integration carried out explicitly using the orthogonality properties of spherical harmonics. The calculation is straightforward and leads to

$$J_m(m\omega_0) = \rho \int_0^{\infty} dk S(k, \tfrac{1}{2}m\omega_0) I(k), \tag{24}$$

where

$$I(k) = 2k^2 \left[\int_0^{\infty} dr\, r^2 F(r) g(r) j_2(kr)\right]^2. \tag{25}$$

For typical nuclear Larmor frequencies $S(k, \omega_0) \simeq S(k, 0)$; thus $J(0) = J_1(\omega_0) = J_2(2\omega_0)$ and, using Eq. (6) the final result for the relaxation rate becomes

$$R_Q = \tfrac{3}{4} f(I)(eQ/\hbar)^2 \rho \int_0^{\infty} dk S(k, 0) I(k). \tag{26}$$

An important feature of Eq. (26) is factorization of the integrand into a term $S(k, 0)$ which describes the liquid dynamics and a term $I(k)$ which depends on the form of the EFG through $F(r)$ in Eq. (25). The EFG function $I(k)$ is an integral transform of $F(r)$ whose structure is determined by the spatial variation of the EFG. It acts as a weighting function determining the relevant k values of modes responsible for quadrupolar relaxation. Some specific examples of $S(k, 0)$ and $I(k)$ will be described in Secs. III and IV.

III. EFG WEIGHTING FUNCTION $I(k)$

In this section some specific forms are described for the EFG weighting function $I(k)$ defined in Eq. (25). Given the radial EFG function $F(r)$ and the pair distribution function $g(r)$ for a specific liquid, $I(k)$ can be obtained directly by numerical integration with respect to r. For purposes of computation the Bessel function is conveniently expressed in terms of ordinary trigonometric functions:

$$j_2(x) = x^{-3}[(3 - x^2)\sin x - 3x\cos x]. \tag{27}$$

In a series of illustrative examples, the simple case of a point charge potential will be considered first and followed by more realistic calculations for liquid rare gases and metals.

A. Point charge potential–magnetic dipolar relaxation

For a simple point charge potential $v(r) = q/r$, Eqs. (5) and (22) yield

$$F(r) = (4\pi/5)^{1/2}(q/r^3). \tag{28}$$

Although a potential of this form would not be expected in a monatomic liquid, it represents an instructive example because of its simplicity. Moreover, it is important to note that $F(r) \propto r^{-3}$ is encountered in the case of magnetic dipolar relaxation since the spatial symmetry of the dipolar interaction is identical to that of the point-charge quadrupolar interaction. Thus the present formulation may be used with relatively minor modifications to describe magnetic dipolar relaxation in monatomic liquids. The equations for magnetic relaxation rates in a system containing a single nuclear spin species are summarized in Appendix B.

The EFG weighting function $I(k)$ for quadrupolar relaxation is shown in Fig. 2(a) for a point charge potential. The integral in Eq. (25) was evaluated using one electronic charge e for q and the experimental $g(r)$ for Ne at 25.5 K.[23] It can be seen that $I(k)$ consists of a series of maxima which decrease rapidly in intensity with increasing k. As a point of reference, the position $k = K_0$ of the principal peak in $S(k)$ is indicated (for Ne, $K_0 = 2.4$ Å^{-1}).

B. Liquid rare gases

The electronic charge distribution of an isolated rare gas atom is spherically symmetric and, therefore, the EFG at the nucleus vanishes. The presence of a neighboring atom distorts the spherical charge distribution and produces an EFG which depends on the relative positions of the two atoms.

Adrian has described a useful, approximate theory for the EFG produced by a single neighboring atom.[24] This calculation treats the EFG as the sum of two contributions: exchange-overlap of the closed shell atomic states and distortion of the spherical configuration by the van der Waals attraction. Naturally, the overlap contribution dominates at small interatomic separations and the van der Waals effect is important at large separations. Adrian[24] showed that the van der Waals term can be approximated in terms of the atomic polarizability α, whereas the overlap EFG can be related to simple overlap integrals between the outermost (n shell) atomic states.[25] His result, expressed in a coordinate system (x', y', z'), in which z' lies along the internuclear axis, is

$$v_{z'z'}(r) = -\tfrac{3}{8}\alpha^2 (v_{zz})_{np} r^{-6} + 2(v_{zz})_{np} \times [\langle ns|n\sigma\rangle^2 + \langle n\sigma|n\sigma\rangle^2 - \langle n\pi|n\pi\rangle^2] , \quad (29)$$

where $(v_{zz})_{np}$ is the EFG produced by an electron in an atomic np state and the overlap integrals $\langle i|j\rangle$ are to be evaluated for two atoms separated by a distance r. Notice that the first or van der Waals term is opposite in sign to the overlap term. Since the (x', y', z') system represents the principal axis system for the EFG tensor of the diatomic pair, and since $\nabla^2 v = 0$, the other components can be obtained from Eq. (29) according to $v_{x'x'} = v_{y'y'} = -\frac{1}{2} v_{z'z'}$.

The radial function $F(r)$ is obtained by transforming to the laboratory (x, y, z) coordinate system and employing Eqs. (5), (8), and (22). The calculation is straightforward and yields

$$F(r) = (v_{zz})_{np} (4\pi/5)^{1/2} [\langle ns|n\sigma\rangle^2 + \langle n\sigma|n\sigma\rangle^2 - \langle n\pi|n\pi\rangle^2 - (3\alpha^2/16 r^6)] . \quad (30)$$

The constants α and $(v_{zz})_{np}$ are available from optical studies of the gaseous phase, whereas the overlap integrals must be determined numerically from a suitable set of atomic wave functions. The sum of overlap integrals in Eq. (30) can be approximated with good accuracy by an exponential around the near-neighbor distance. Therefore, for purposes of calculation, Eq. (30) may be written in the form

$$F(r) = a e^{-k_0 r} - b r^{-6} , \quad (31)$$

where a, b, and k_0 are to be determined from Eq. (30) and a fit to calculated overlap integrals.

In order to examine the theory for a liquid rare gas, the functions $F(r)$ and $I(k)$ were evaluated for liquid Ne. The overlap integrals were computed[26] for various values of r over the range 2.6–3.6 Å using basis functions given by Huzinaga.[27] These integrals together with the experimental values[28,29] $(v_{zz})_{2p} = 3.31 \times 10^{-8}$ statC/Å^3 and $\alpha = 0.392$ Å^3 yield the following values for the parameters in Eq. (31): $a = 8.42 \times 10^{-5}$ statC/Å^3, $b = 0.15 \times 10^{-8}$ statC Å^3, and $k_0 = 5.54$ Å^{-1}. The weighting function $I(k)$ for liquid Ne at 25.5 K is shown in Fig. 2(b). The form of $I(k)$ is qualitatively similar to that obtained for the point charge EFG [Fig. 2(a)]. However, two important differences are evident.

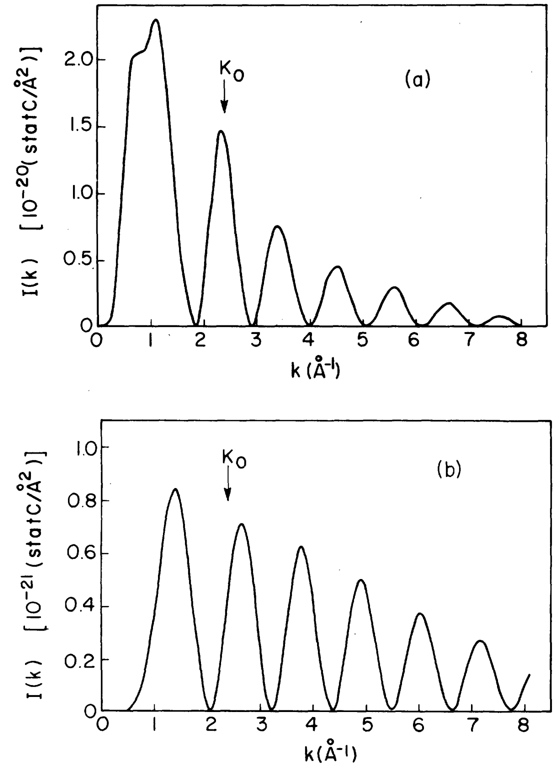

FIG. 2. EFG weighting function $I(k)$ evaluated from Eq. (25) for liquid Ne at 25.5 K. (a) Fictitious point charge EFG for one electronic charge. $I(k)$ for a point charge differs only by a constant from the analogous function $I_D(k)$ for magnetic dipolar relaxation. (b) Exchange–van der Waals EFG described by Eq. (31). Vertical arrows indicate positions (K_0) of main peaks in the liquid structure factor $S(k)$.

First, the point charge EFG for one electronic charge leads to $I(k)$ roughly one order of magnitude greater than the exchange–van der Waals form. Second, $I(k)$ for the exchange–van der Waals EFG has relatively more intensity at high k values than the point-charge case. This reflects the stronger r dependence of the exchange-van der Waals EFG.

As an independent check on the accuracy of the Adrian model, the function $F(r)$ was computed directly using molecular wave functions constructed from the same atomic basis functions used for the overlap integrals.[30] The results of these calculations are compared with Eq. (31) at three r values in Table I. The two calculations agree very well, within 10%, for $r = 3.0$ Å, while the agreement is less satisfactory at the extreme r values checked. At $r = 3.6$ Å, the two methods give results of opposite signs, reflecting the fact that the molecular wave functions do not include electronic correlations responsible for the negative van der Waals term in Adrian's model. Nevertheless, the agreement in the region near the main peak of $g(r)$ which dominates the integral in Eq. (25) gives confidence that Adrian's model is sufficiently accurate for present purposes.

C. Liquid metals

Calculation of local electric field gradients in metals is a complex problem and considerable effort has been devoted to sophisticated and detailed computations for metallic crystals.[31] In general, the EFG contribution is determined for various electronic eigenstates using wave functions obtained with a suitable potential. The total field gradient is then obtained by adding the electronic contributions to the ionic contribution and performing a lattice sum. For a liquid metal, where neither the electronic eigenstates nor the ionic positions are precisely known such a procedure seems hopeless at this stage. A simpler approach is to attempt to determine some effective ionic potential $v(r)$ which includes the screening effects of the conduction electrons and from which the radial EFG function $F(r)$ can be obtained by differentiation using Eq. (22).

TABLE I. Radial EFG function $F(r)$ for Ne from exchange–Van der Waals model (E-V) and molecular orbital calculations (MO).

r(Å)	$F(r)$ E-V	10^{-12} statC/Å^3 MO
2.6	52.8	34.91
3.0	3.82	4.21
3.6	−0.643	0.712

The simplest potential function, and the one used in previous work,[17] is the asymptotic form of the screened Coulomb potential

$$v(r) = C\cos(2k_F r)/(2k_F r)^3, \qquad (32)$$

where k_F is the Fermi wave vector and C is a strength parameter. For a potential of this form, the radial function is

$$F(r) = C'(4\pi/45)^{1/2}(2k_F)^2 \times\{7(2k_F r)\sin(2k_F r) + [15 - (2k_F r)^2]\cos(2k_F r)/(2k_F r)^5\}, \qquad (33)$$

where C' contains a factor to account for the quadrupolar antishielding effects of the core electrons.[32]

The potential given by Eq. (32) is strictly correct only in the limit of large r. Its use at the near-neighbor distance where the largest contribution to the EFG arises is therefore questionable. One way to partially circumvent this difficulty was devised by Sholl,[17] who determined the constant C' by comparison with the known static EFG in the crystal. This procedure amounts to assuming that the spatial variation of $v(r)$ and $F(r)$ in the vicinity of the near neighbor distance are correctly described by Eqs. (32) and (33) and adjusting the strength C' to agree with experiment. The method is, of course, limited to metals having a noncubic crystal structure for which the EFG tensor may be directly measured from nuclear quadrupole splitting. In spite of these drawbacks, the normalized asymptotic form remains attractive as a first approximation to the problem because of its relatively simple analytic form.

Once a potential $v(r)$ is given, the radial function $F(r)$ and the weighting function $I(k)$ may be computed as before using Eqs. (22) and (25) and an appropriate pair distribution function $g(r)$. The form of $I(k)$ for the asymptotic screened Coulomb potential is illustrated in Fig. 3 for liquid Ga at 293 K. Sholl's value[17] $C' = 3.469\times10^{-8}$ statC/Å was used together with an experimental $g(r)$ obtained from x-ray and neutron diffraction data.[33] It is evident from this plot that a major contribution to R_Q in a metal comes from $k \sim 2k_F$, where the two largest peaks in $I(k)$ occur. This has the interesting consequence that for metals of differing valence, and hence differing values of k_F, quadrupolar relaxation samples dynamical modes of somewhat different k values. It is worth emphasizing, however, that the detailed shape of $I(k)$ is highly sensitive to the spatial variation of $v(r)$, since $F(r)$ depends on its second derivative. In light of the uncertainty concerning the correct choice of potential, the form of $I(k)$ for liquid metals cannot be considered to be as firmly established as for the liquid rare gases.

IV. DYNAMIC STRUCTURE FACTOR $S(k,0)$

The dynamic structure factors $S_s(k, \omega)$ and $S(k, \omega)$ describe the basic liquid dynamics for single-particle and collective motions, respectively.[34] These functions are directly measurable by means of various scattering experiments. The cross section for incoherent scattering of thermal neutrons, for example, is proportional to $S_s(k, \omega)$, whereas $S(k, \omega)$ determines the cross section for coherent scattering of neutrons or light. The function $S(k, 0)$ which determines the quadrupolar relaxation rate describes the amplitude of the so-called "quasielastic" peak of $S(k, \omega)$ for various values of k.

It is instructive to make some comparisons here with the earlier work of Sholl.[17] In that theory, both the two- and three-particle correlations were described in terms of the "self" part of the time-dependent pair-distribution function for single particle diffusion:

$$G_s(\vec{r}, t) = (4\pi D t)^{-3/2} e^{-r^2/4Dt} . \tag{34}$$

This has the Fourier transform

$$S_s(k, \omega) = \frac{1}{\pi} \frac{Dk^2}{\omega^2 + (Dk^2)^2} . \tag{35}$$

If we take the $\omega = 0$ limit and substitute $S_s(k, 0)$ for $S(k, 0)$ in Eq. (26), we find

$$R_Q = \tfrac{3}{4} f(I)(eQ/\hbar)^2(\rho/\pi D) \int dk\, (1/k^2) I(k), \tag{36}$$

which is closely similar to the two-particle (I_1) term in Sholl's theory.[35] The present theory differs from Sholl's mainly in that both two- and three-particle correlations are included in a single term governed by $S(k, \omega)$.

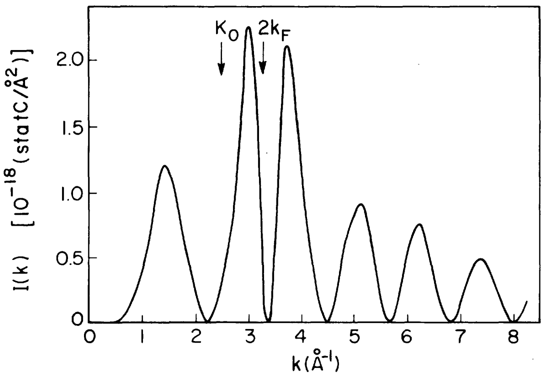

FIG. 3. EFG weighting function $I(k)$ for asymptotic form of the screened Coulomb potential evaluated for liquid Ga at 293 K. The EFG is given by Eq. (33). Vertical arrows indicate positions of main liquid structure factor peak (K_0) and twice the Fermi wave vector ($2k_F$). Note that $I(k)$ gives maximum weight to k values near $2k_F$ although a node occurs at precisely $k = 2k_F$.

The nature of $S(k, \omega)$ for liquid rare gases and metals has been studied by experiment, molecular dynamics calculations, and theory.[36] The question of the existence of well-defined vibrational collective modes at high frequency has, in particular, received much attention.[37–41] Such modes correspond to peaks in $S(k, \omega)$ at finite ω values as exemplified by the well-known Brillouin doublet observed in light scattering for $k \ll K_0$. Neutron scattering at higher k values ($k \lesssim K_0$) indicate the presence of such peaks in liquid metals[37–41] such as Pb and Rb, whereas these are absent in liquid Ar and Ne.[22,42] The evidence indicates that collective modes at finite frequency are heavily overdamped for k values around K_0 where their contribution to $S(k, \omega)$ merges with the central $\omega = 0$ peak. Nevertheless, they may remain important for nuclear quadrupolar relaxation since they modify the value of $S(k, 0)$ in this range where the weighting function $I(k)$ has large amplitude.

In principle R_Q could be calculated directly from neutron data for $S(k, 0)$ using Eq. (26). Unfortunately, precise data are not yet available over wide ranges of temperature and k values for those liquids which have been studied by nuclear quadrupolar relaxation. On the other hand, there exist some simple theoretical forms which have been found to give good agreement where the neutron data do exist. In each case the function $S(k, 0)$ can be determined from the static structure factor $S(k)$. The latter is available for many more liquids and temperatures than $S(k, 0)$ and, in particular, has been measured for Ne and Ga whose quadrupolar relaxation rates will be considered shortly.

A. Liquid rare gases

These liquids, particularly liquid Ar, have been the most extensively studied from the point of view of their liquid dynamics and many theories of $S(k, \omega)$ have been developed. Pathak and Singwi[43] described a mean field approximation for the density response function having the virtue that their $S(k, 0)$ satisfies certain conditions on the frequency moments out to the fourth moment. The theory yields results in good agreement with experiments for liquid Ar.[22] Their expression for $S(k, 0)$ takes a relatively simple form:

$$S(k, 0) = \frac{1}{2\pi^{1/2}} \left(\frac{M}{k_B T}\right)^{1/2} \frac{[S(k)]^2}{k} \times \left[3 - \frac{1}{S(k)} + \frac{\rho P_4(k)}{k_B T}\right]^{1/2}, \tag{37}$$

where

$$P_4(k) = \int d\vec{r}\, g(r)\, \frac{(1-\cos k_z r)}{k^2}\, \frac{\partial^2 \Phi(r)}{\partial z^2} \tag{38}$$

and $\Phi(r)$ is the interatomic potential. Lovesey[44] presented an extension of the low-q hydrodynamic theory which also satisfies the moment conditions. His expression for $S(k, 0)$ is identical with Eq. (37) obtained by Pathak and Singwi.[45]

The Pathak-Singwi-Lovesey result was obtained in the high-temperature classical approximation which is valid for liquid Ar. For the case of Ne, Kerr and Singwi showed that the quantum corrections are not negligible.[46] However, for k values out to about $2K_0$, these corrections are less than about 20%, and, in the important region around K_0, quantum effects are substantially smaller. For the present discussion we shall use the simpler, classical version of the theory which is sufficiently accurate for our purpose.

The specific form of $S(k, 0)$ is illustrated in Fig. 4 for Ne at 25.5 K. In evaluating Eq. (37), the x-ray data of Stirpe and Tompson were used for $S(k)$ and $g(r)$.[47] The potential $\Phi(r)$ used to evaluate $P_4(k)$ was a Lennard-Jones potential with $\sigma = 2.75$ Å and $\epsilon = 49.2 \times 10^{-16}$ erg for Ne.[48] It is evident that the form of $S(k, 0)$ is dominated by a strong peak at K_0 with smaller, broader peaks occurring at higher k values. A comparison of Fig. 4 with Fig. 2(b) shows that the main contribution to R_Q comes from modes in the range $2 \lesssim k \lesssim 4$ Å^{-1}, where both $S(k, 0)$ and $I(k)$ have large amplitudes. Note that the large peak in $I(k)$ at 1.4 Å^{-1} has little effect owing to the small value of $S(k, 0)$ in this range.

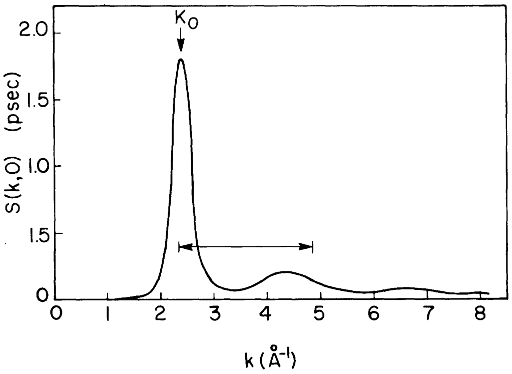

FIG. 4. Elastic ($\omega = 0$) limit of dynamic liquid structure factor $S(k,\omega)$ vs k for liquid Ne at 25.5 K. $S(k, 0)$ was evaluated from Eqs. (37) and (38) using experimental data for the static structure factor $S(k)$ given in Ref. 23. Vertical arrow indicates position of main liquid structure factor peak (K_0). Horizontal arrow indicates range over which relaxation rate integral in Eq. (26) increases from 10% to 90% of its final value.

B. Liquid metals

In principle the Pathak-Singwi-Lovesey form could be used for $S(k, 0)$ in liquid metals as well as rare gases. However, evaluation of the fourth-moment term $P_4(k)$ is complicated by lack of accurate knowledge of the interparticle potential $\Phi(r)$. Since second derivative $\partial^2\Phi(r)/\partial z^2$ enters in Eq. (38), the result may be expected to depend sensitively on the detailed r dependence of the potential. It therefore seems advisable to take a more empirical approach and use a parameterized model which can be adjusted to fit the neutron data where they exist.

There is evidence for qualitative differences between $S(k, \omega)$ in liquid rare gases and metals.[39,40] Neutron experiments suggest the presence of underdamped modes at finite frequency for Pb and Rb when $k \lesssim k_0$, whereas no such evidence has been found for liquid Ar and Ne. Because of the longer range of the potential in metals it is not surprising that cooperative effects are stronger in this case. In the particular case of Pb, Cocking and Egelstaff[37] assumed a general parameterized form for $S(k, \omega)$ which they adjusted to fit their time-of-flight neutron spectra. In the $\omega = 0$ limit, their model reduces to

$$S(k, 0) = \frac{N_{12}}{\pi} \left(\frac{M}{k_B T}\right)^{1/2} \frac{[S(k)]^{3/2}}{k}, \tag{39}$$

where N_{12} is determined by fitting to the neutron data ($N_{12} = N_1/N_2$ in the notation of Ref. 37). In the case of Pb, $N_{12} = 3$.

Since the magnitudes of $S(k, 0)$ and $S(k)$ near the melting point (T_m) cannot differ greatly between different simple liquids, it is reasonable to estimate N_{12} for Ga by assuming $(N_{12}/K_0)(M/T_m)^{1/2}$ to be constant. Then, if $N_{12}(\text{Pb}) = 3$, this method gives $N_{12}(\text{Ga}) \simeq 4.6$. Alternatively, Eq. (39) can be fitted to experimental data for $S(k, 0)$ in the range of k values where they are available (near K_0) and Eq. (39) can be regarded as a means of extrapolating the data beyond the range of the measurements. This procedure is illustrated in Fig. 5, where Eq. (39) is plotted together with the experimental values of $S(k, 0)$ measured by Chen, Lefevre, and Yip.[49] The value $N_{12} = 4.9$ chosen to give a reasonably good fit to the data agrees well with the estimate based on the Pb results. Note however that Eq. (39) tends to deemphasize somewhat the pronounced "shoulder" on the high-k side of the main diffraction peak. While potentially important for precise calculations, this deficiency of Cocking and Egelstaff's model will be neglected for the present purposes.

Recalling that $I(k)$ is largest near $k = 2k_F$ for the asymptotic screened Coulomb potential ($3 \lesssim k \lesssim 4$ Å^{-1}), note that R_Q is dominated by modes having k values somewhat higher then K_0. Vibrational modes, if present in this range, are overdamped. Nevertheless, as has already been pointed out, these modes may yet affect the value of $S(k, 0)$. Finally, it should now seem no surprise that the temperature dependence of R_Q does not agree well with predictions based on Eq. (35) since this low-k form cannot provide an adequate description of the liquid dynamics for $k \sim 2k_F$.[50]

V. NUMERICAL RESULTS FOR RELAXATION RATE IN LIQUID Ne AND Ga

As a test of the theory the relaxation rate was calculated for a liquid rare gas (Ne) and a liquid metal (Ga) for which quadrupolar relaxation data were available. Although quadrupolar relaxation rates have been measured for three liquid rare gases[1-3] (Ne, Kr, and Xe), Ne was chosen because there exist tabulated data for $S(k)$ and $g(r)$ over a wide temperature range.[47] For Ga there exist good NMR data and precise x-ray and neutron diffraction measurements of $S(k)$ near T_m and in the supercooled state.[33,51,52] Although $S(k)$ has, in fact, been measured to high temperatures by Lashko and Poltavtsev, these data were not available in a form suitable for accurate numerical computation.[53]

A. Liquid Ne^{21}

The relaxation rate for liquid Ne^{21} at 25.5 K was evaluated numerically from Eq. (26) using the values $I = \frac{3}{2}$, $Q = 0.093$ Å^3, and $\rho = 0.0354$ Å^{-3}. The structure factor $S(k, 0)$ was calculated as for Fig. 4 using the Pathak-Singwi-Lovesey expression, Eq. (37), and the EFG weighting function $I(k)$ was calculated with Eq. (31) for $F(r)$ as discussed in Sec. III B. The result is

$$R_Q^{21} = 0.0310 \text{ sec}^{-1} \quad \text{(theory)},$$

which can be compared with the value measured by Henry and Norberg[2] at 25.3 K:

$$R_Q^{21} = 0.040 \text{ sec}^{-1} \quad \text{(experiment)}.$$

The success of the theory in giving the magnitude of the relaxation rate within 25% is encouraging. The discrepancy, explainable by only a 12% error in the EFG, is quite reasonable given the residual uncertainty in the EFG and the various approximations of the general theory.

The temperature dependence of R_Q provides a more stringent test of the basic theory since it is directly dependent on the liquid dynamics. In order to compare with experiment, R_Q was calculated at two additional temperatures for which $S(k)$ data are available and the results normalized to the R_Q data at the lowest temperature. The resulting temperature variation is shown in Fig. 6 together with the experimental data. Also shown is the variation of ρ/D which is the predominant temperature dependent factor when the liquid dynamics are described in terms of macroscopic single-particle diffusion. It is clear that the present theory is in quite satisfactory agreement over the range of the data although the theoretical curve does not lie fully within the experimental error. There is no question that the present model represents a substantially improved approximation over earlier theories.

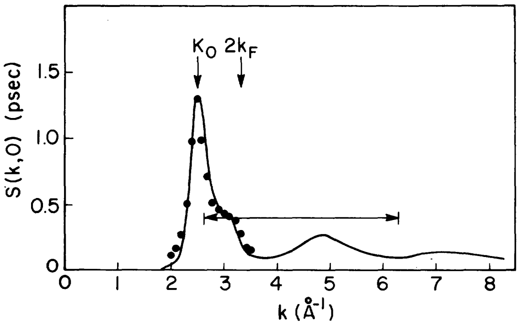

FIG. 5. Elastic ($\omega = 0$) limit of dynamic liquid structure factor $S(k, \omega)$ vs k for liquid Ga at 293 K. $S(k, 0)$ was evaluated from Eq. (39) using $N_{12} = 4.9$ and data for $S(k)$ given in Ref. 33. Closed circles denote experimental values of $S(k, 0)$ obtained with neutron scattering by Chen, Lefevre, and Yip (Ref. 49). Vertical arrow marks the main liquid structure factor peak at K_0. Horizontal arrow indicates range over which relaxation rate integral in Eq. (26) increases from 10% to 90% of its final value.

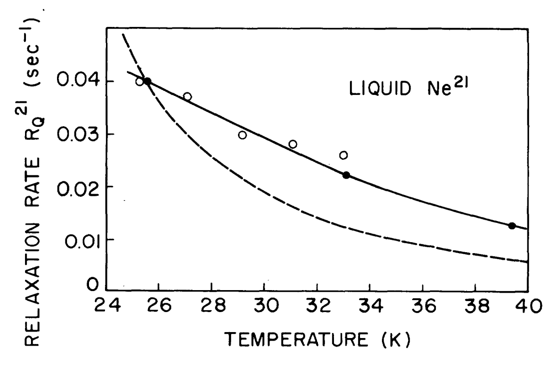

FIG. 6. Quadrupolar relaxation rate R_Q^{21} vs temperature for Ne^{21} in liquid Ne. Open circles denote data of Henry and Norberg (Ref. 2). Solid curve denotes temperature variation predicted by present theory from calculations at 25.5, 33.1, and 39.4 K. Dashed curve denotes characteristic temperature dependence for single-particle diffusion described by Eq. (1). Both theoretical curves were normalized to data at 25.5 K.

B. Liquid Ga^{69}

The relaxation rate for Ga^{69} was evaluated at a single temperature (293 K) using $I=\frac{3}{2}$, $Q=0.180$ $\mathrm{\AA}^3$, and $\rho=0.05272$ $\mathrm{\AA}^{-3}$. The function $I(k)$ was computed using the asymptotic screened Coulomb potential and Sholl's strength parameter C' as discussed in Sec. III C. The Cocking and Egelstaff model for $S(k,0)$ was used with $N_{12}=4.9$ as described in Sec. IV B. The result is

$$R_Q^{69}=331\ \mathrm{sec}^{-1}\quad \text{(theory)}.$$

The most precise experimental value available is[54]

$$R_Q^{69}=350\pm 11\ \mathrm{sec}^{-1}\quad \text{(experiment)}.$$

Just as for Ne the agreement in magnitude is very good, although it must be remembered that the potential was normalized to the known EFG in the crystal to obtain the parameter C'. Nevertheless, the agreement is much better than obtained by Sholl,[17] who found values of 149 or 500 sec^{-1}, depending on whether or not he included the three-particle (I_2) term in Eq. (2). Since both calculations use the same potential it would appear that the present theory incorporates a better approximation of the liquid dynamics.

VI. SUMMARY AND CONCLUSIONS

A new theory of nuclear electric quadrupolar relaxation in monatomic liquids has been described. The theory is based on an approximation expressing the joint probability function $P(\vec{r}_0, 0; \vec{r}_1, t)$ in terms of the full van Hove time-dependent pair distribution function. This approximation leads directly to a simple expression for the relaxation rate in terms of an integral over $S(k,0)$ multiplied by a weighting function $I(k)$. This formulation therefore achieves factorization of the liquid dynamics, contained in $S(k,0)$, and the EFG whose radial variation determines $I(k)$. Comparison of $I(k)$ and $S(k,0)$ for realistic cases shows that the major contribution to quadrupolar relaxation comes from low frequency modes having $k \gtrsim K_0$. For liquid metals, in particular, an important contribution arises from $k \sim 2k_F$. For these relatively high q values collective motions of the ions are important and it is not correct to attribute quadrupolar relaxation to single-particle diffusion as has been done previously.

Numerical calculations for Ne and Ga near their melting points are very encouraging and agree with the observed relaxation rates within about 25% for Ne and 6% for Ga. Uncertainty in the exact form of $I(k)$ for Ga suggests, however, that we should be cautious of fortuitous agreement for that case. Nevertheless the Ga results are substantially better than achieved previously using the diffusion model and the same EFG function. The theory also gives good agreement for the temperature dependence of the relaxation in liquid Ne. Success of the theory for such diverse liquids as Ne and Ga lends confidence that it provides an accurate description of the coupling of nuclei to microscopic liquid dynamics.

The sharply peaked character of $I(k)$ means that the relaxation rate is fairly sensitive to the form of $S(k,0)$. In the case of rare gases, where further refinements of the precision of $I(k)$ appear possible, quadrupolar relaxation data may be useful as a means of testing model forms of $S(k,0)$ in situations for which neutron data are absent. For metals, there is an obvious need for better knowledge of the EFG functions $F(r)$ and $I(k)$ before such a procedure can be trusted. Conversely, if $S(k,0)$ is known, quadrupolar relaxation provides a means of testing various forms of the potential and EFG. For the determination of $S(k,0)$ or $S(k,\omega)$ it is clearly preferable to use a spectroscopic technique such as neutron scattering when such experiments are practical since they provide more detailed information than an integral method such as quadrupolar relaxation. However, the relative simplicity, low cost and versatility of NMR experiments suggest a useful role for quadrupolar relaxation data as an alternative means of exploring liquid dynamics in monatomic liquids.

ACKNOWLEDGMENTS

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APPENDIX A: JUSTIFICATION OF THE "EQUAL WIDTH" APPROXIMATION

This appendix describes the correction to the approximation of Eq. (14) when $S_s(k,\omega)$ and $S(k,\omega)$ do not have the same Lorentzian widths and summarizes the effect of this correction on the calculation of the relaxation rate R_Q.

Consider a double integral of the following form which appears in Eqs. (12) and (14):

$$I=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} d\omega\, d\omega'\, e^{i(\omega+\omega')t} f(\omega) g(\omega'), \tag{A1}$$

where

$$g(\omega') = \frac{1}{\pi}\,\frac{\Delta}{\Delta^2+\omega^2}\,, \tag{A2}$$

$$f(\omega) = \frac{c}{\pi}\,\frac{\delta}{\delta^2+\omega^2}\,. \tag{A3}$$

Note that, in analogy with $S_s(k,\omega)$ and $S(k,\omega)$, $g(\omega')$ and $f(\omega)$ are normalized, respectively, to unity and to a constant c. Substitution of Eqs. (A2) and (A3) into (A1) and integrating over ω and ω' leads to

$$I = ce^{-(2\delta+\epsilon)|t|} = e^{-\epsilon|t|}\int d\omega\, e^{i2\omega t} f(\omega), \tag{A4}$$

where $\epsilon \equiv \Delta - \delta$. When $\epsilon = 0$, Eq. (A4) reduces to Eq. (14).

When Eq. (A4) is employed in Eq. (12), we find

$$\int d\vec{r}\, G_s(\vec{r},t)\, G(\vec{r}+\vec{r}_1-\vec{r}_0,t) = \rho + e^{-\epsilon|t|} \times [G(\vec{r},2t)-\rho] \tag{A5}$$

and hence, from Eq. (10)

$$P(\vec{r}_0,0;\,\vec{r}_1,t) = \rho g(r_0)\, g(r_1)\, e^{-\epsilon|t|} \times [G(\vec{r},2t)+\rho(e^{\epsilon|t|}-1)]\,. \tag{A6}$$

The joint probability function of Eq. (A6) may now be used to calculate the spectral density functions as described in Sec. II C. It follows directly that Eq. (24) becomes

$$J_m(m\omega_0) = \rho\int_0^\infty dk\, I(k) \times \int_{-\infty}^{\infty} d\omega\, S(k,\omega)\, \frac{\epsilon/2\pi}{\epsilon/2+(\omega-\frac{1}{2}m\omega_0)^2}\,. \tag{A7}$$

Thus the δ function $\delta(\omega-\frac{1}{2}m\omega_0)$, which leads to the factor $S(k,\frac{1}{2}m\omega_0)$ when $\epsilon = 0$, has been replaced by a Lorentzian distribution of width $\frac{1}{2}\epsilon$. It is easily verified that for typical values[22] $\epsilon/\delta \simeq 0.3$, the δ function approximation is accurate to about 2% for the value of $J_m(m\omega_0)$.

APPENDIX B: MAGNETIC DIPOLAR RELAXATION FOR A SINGLE SPIN SPECIES

In Sec. III A it is pointed out that the form of $F(r)$, and hence $I(k)$, are identical for the point charge quadrupolar interaction and the magnetic dipole-dipole interaction. In this appendix the expression for the dipolar relaxation rate will be derived in the notation of the quadrupolar relaxation theory in order to demonstrate the correspondence between these two kinds of relaxation process. For simplicity, the system will be assumed to contain only one magnetic nuclear species with fractional abundance f_n.

The Hamiltonian describing the mutual dipolar interactions of a system of nuclei with spin I and gyromagnetic ratio γ_n may be written in a form analogous to Eqs. (3)–(5):

$$\mathcal{H}_D(t) = \sum_{ij}\sum_{m=-2}^{2} D_{ij}^{m} F_{ij}^{-m}(t), \tag{B1}$$

where the sum is taken over all pairs (i,j) of interacting nuclei. The spin functions D_{ij}^m and "lattice functions" F_{ij} are

$$D_{ij}^{0} = B(\vec{I}^{i}\cdot\vec{I}^{j} - 3I_z^i I_z^j), \tag{B2a}$$

$$D_{ij}^{\pm 1} = \sqrt{\tfrac{3}{2}}\, B(I_z^i I_\pm^j + I_\pm^i I_z^j), \tag{B2b}$$

$$D_{ij}^{\pm 2} = \sqrt{\tfrac{3}{2}}\, B I_\pm^i I_\pm^j, \tag{B2c}$$

$$F_{ij}^{\pm m} = (4\pi/5)^{1/2}(\mp 1)^m (1/r_{ij}^3)\, Y_2^{\pm m}(\theta_{ij},\varphi_{ij}), \tag{B3}$$

and $B = \gamma_n^2\hbar^2$. Notice that $F_{ij}^{\pm m}(\vec{r})$ is proportional to $v^{\pm m}(\vec{r})$ given by Eqs. (22) and (28) for the point charge quadrupolar interaction.

In the limit of "extreme narrowing" the density matrix method of Abragam[55] gives the following expression for the relaxation rate:

$$\frac{1}{T_1} = \Big(2\hbar^2\sum_i \{I_z^i\}\Big)^{-1} \sum_m\sum_{ijj} J_{ijj'}^m(0)\, C_{ijj'}^m\,, \tag{B4}$$

where

$$J_{ijj}^m(\omega) = \int_{-\infty}^{\infty} dt\, e^{-i\omega t}\langle F_{ij'}^m(t)\, F_{ij}^{-m}(0)\rangle_{\text{av}}\,, \tag{B5}$$

$$C_{ijj'}^m = \{[D_{ij}^m,[D_{ij'}^{-m},I_z^i]]\}\,, \tag{B6}$$

and the curly brackets { } indicate that an expectation value is to be taken over the density matrix of the system.

The form of Eq. (B4) demonstrates an important distinction between quadrupolar and dipolar relaxation. The operators D_{ij}^m involve the spins of *both* the "nucleus of interest," say (i), and the neighbor (j) in contrast to the operators Q^m which depend only on the spin of the nucleus of interest. This leads to the dependence of $C_{ijj'}^m$ on j and j'. Now because $C_{ijj}^m \neq C_{ijj'}^m$ when $j \neq j'$, it is not possible to combine the two- and three-particle contributions to $1/T_1$ as could be done for the quadrupolar case. In fact, as Titman[56] has recently pointed out $C_{ijj'}^m \ll C_{ijj}^m$ so that the two particle terms dominate the dipolar relaxation rate. Then letting $C_{ijj'}^m = C_{ijj}^m\delta_{jj'}$, the commutators and expectation values may be evaluated as outlined by Abragam[57] to yield

$$R_D = \frac{1}{T_1} = 5\gamma_n^4\hbar^2 I(I+1)\, J(0), \tag{B7}$$

where

$$J(0) = \sum_j J_{jj}^1(0) = \sum_j J_{jj}^2(0), \tag{B8}$$

$$\sum_j J^m_{jj}(\omega) = \int_{-\infty}^{\infty} dt\, e^{-i\omega t} \int\int d\vec{r}_0\, d\vec{r}\, P_s(\vec{r}_0, 0; \vec{r}_1, t) \times F^m(\vec{r}_1) F^{-m}(\vec{r}_0). \tag{B9}$$

The subscript s on $P_s(\vec{r}_0, 0; \vec{r}_1, t)$ emphasizes that the atom at relative position $\vec{r}_1$ at time t is the same as initially at $\vec{r}_0$.

Evaluation of $J(0)$ proceeds in exactly the same manner as described in Sec. II B and II C, except that $G_s(\vec{r}_1 - \vec{r}_0, 2t)$ appears in the analogue of Eq. (16) in place at $G(\vec{r} - \vec{r}_0, 2t)$. The spectral density function is

$$J(0) = f_n \rho \int dk\, S_s(k, 0) I_D(k), \tag{B10}$$

where

$$I_D(k) = (4\pi/5) k^2 \left[\int_0^{\infty} dr\, (1/r)\, g(r) j_2(kr) \right]^2 . \tag{B11}$$

Finally, on substitution of Eq. (B10) in Eq. (B7), the expression for the relaxation rate is obtained:

$$R_D = 5\gamma_n^4 \hbar^2 I(I+1) f_n \rho \int dk\, S_s(k, 0) I_D(k). \tag{B12}$$

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