THE INFLUENCE OF HYDRODYNAMIC INTERACTION ON THE INTERMOLECULAR CONTRIBUTION TO MAGNETIC RELAXATION TIMES IN LIQUIDS

PHYSICS

1967

SovietRxiv

Abstract

Full Text

UDC 538.69.083.2:539

PHYSICS

T. N. KHAZANOVICH

THE INFLUENCE OF HYDRODYNAMIC INTERACTION ON THE INTERMOLECULAR CONTRIBUTION TO MAGNETIC RELAXATION TIMES IN LIQUIDS

(Presented by Academician V. N. Kondrat' ev on 21 XI 1966)

From the theory of magnetic resonance (see, for example, (^{1,2})) it follows that relaxation times are expressed in terms of time-correlation functions of harmonic polynomials. In the case of magnetic dipole-dipole interaction, for example, correlation functions of $Y_2^m(\theta, \varphi)r^{-3}$ arise, where Y_2^m is a spherical function and r, θ, φ are the polar coordinates of the vector joining the interacting spins. When these spins belong to different molecules, the corresponding correlation functions refer to the intermolecular contribution to the relaxation times. Beginning with Bloembergen, Purcell, and Pound (^{3}), most authors have calculated the intermolecular contribution by using the assumption that the relative motion of molecules is diffusion with diffusion coefficient $2D$, where D is the self-diffusion coefficient; in other words, it is assumed that the probability density for the vector $\mathbf{r}$ satisfies the diffusion equation

$$\partial W(\mathbf{r}, t)/dt = 2D\Delta W(\mathbf{r}, t). \tag{1}$$

Equation (1) is valid only if the motions of the molecules are independent. However, molecular motion in liquids is cooperative, which means that it is impossible for any molecule to move without a simultaneous, coordinated displacement of its neighbors. Consequently, the assumption of independence of motions in a liquid is illegitimate. But this does not mean that a diffusion description of molecular motion is illegitimate. Indeed, diffusion equations, or, as they are also called, Smoluchowski equations, are valid for time intervals much greater than the momentum relaxation time $\sim mD/kT$, where m is the mass of the molecule, k is Boltzmann' s constant, and T is the absolute temperature. The correlation time for the intermolecular contribution is, in order of magnitude, equal to a^2/D, where a is the molecular radius (see, for example, (^{2})). In most ordinary liquids the momentum relaxation time is 10^2–10^3 times smaller than the correlation time. It follows that, for calculating the correlation time, one may use a diffusion equation in which, however, the cooperativity of molecular motion must be taken into account. The general form of such an equation is

$$\frac{\partial \rho(\mathbf{r},t)}{\partial t} = 2D\frac{\partial}{\partial r_\alpha}\Phi_{\alpha\beta}\left(\frac{\partial \rho}{\partial r_\beta} + \frac{1}{kT}\frac{\partial V}{\partial r_\beta}\rho\right), \tag{2}$$

where $\Phi_{\alpha\beta}$ is a tensor that takes into account the interdependence of the motions, V is the effective potential of interaction of the molecules, and summation from 1 to 3 is carried out over repeated indices. An equation of type (2) for monatomic molecules was derived by Green (^{4}) and, for more general systems, by Zwanzig (^{5}).

We assume that the cooperativity of molecular motion can be qualitatively described by the hydrodynamic interaction, long known in the theory of polymer solutions (see, for example, (^{6})).

Hydrodynamic interaction takes into account the emergence of a velocity field around a moving particle. If the Stokes solution is adopted for the velocity field, then the tensor $\Phi_{\alpha\beta}$ will have the form:

$$\Phi_{\alpha\beta} = \varphi_1\delta_{\alpha\beta} - \varphi_2\frac{3r_\alpha r_\beta}{4r^2}, \tag{3}$$

where

$$\varphi_1 = 1 - \frac{3}{4}\frac{a}{r} - \frac{a^3}{r^3}, \qquad \varphi_2 = \frac{a}{r} - \frac{a^3}{r^3}.$$

We shall restrict ourselves only to the dipole-dipole interaction. In this case the desired correlation function has the form:

$$K(t) = \int dr\, r^{-3} Y_2^m \rho_m(\mathbf{r},t), \tag{4}$$

where $\rho_m(\mathbf{r},t)$ is the solution of equation (2) with the initial condition:

$$\rho_m(\mathbf{r},0) = r^{-3} Y_2^{m*}\rho_0(r),$$

where $\rho_0(r) = N\exp(-V/kT)/\int dr\,\exp(-V/kT)$, ($N$ is the number density of molecules) is the radial distribution function (cf. (7).)

Introduce a new unknown function

$$\rho_m(\mathbf{r},t) = \rho_0^{1/2} W_m(\mathbf{r},t)$$

and, taking into account that the molecules interact strongly (V changes rapidly) over an interval of change in r small in comparison with the order a that is of interest to us, we shall neglect second derivatives of V and the squares of first derivatives and terms containing products $(\partial V/\partial r_\alpha)(\partial \Phi_{\alpha\beta}/\partial r_\beta)$. Then for W_m one obtains an equation not containing V:

$$\frac{\partial W_m}{\partial t} = 2D\frac{\partial}{\partial r_\alpha}\Phi_{\alpha\beta}\frac{\partial W_m}{\partial r_\beta}. \tag{5}$$

The approximation leading to (5) fully corresponds to the constant-acceleration approximation of Oppenheim and Bloom ([8]).

We shall solve equation (5) by a variational method. Introduce the Laplace transform

$$\widetilde{W}_m(\mathbf{r}, p) = \int_0^\infty e^{-pt} W_m(\mathbf{r}, t)\, dt.$$

The stationarity condition of the functional

$$\Omega = \int dr \left[2D\Phi_{\alpha\beta}\frac{\partial \widetilde{W}_m}{\partial r_\alpha}\frac{\partial \widetilde{W}^*_m}{\partial r_\beta} + p|\widetilde{W}_m|^2 - \left(Y_2^{m*}\widetilde{W}_m + Y_2^m\widetilde{W}^*_m\right) r^{-3}\rho_0^{1/2}(r)\right] \tag{6}$$

is equivalent to the Laplace transform of equation (5). We choose the trial function in the form of the solution of equation (1) with the initial condition $W_m(\mathbf{r}, 0) = Y_2^{m*} r^{-3}\rho_0^{1/2}(r)$:

$$\widetilde{W}_m(\mathbf{r}, p) = \frac{Y_2^{m*}}{r^{1/2}} \int_0^\infty dx\, \frac{\rho_0^{1/2}(x)}{x^{3/2}} \int_0^\infty dy\, \frac{y J_{5/2}(xy) J_{5/2}(yr)}{2d(p)y^2 + p}, \tag{7}$$

where $J_n(x)$ is the Bessel function and $d(p)$ is a variational parameter having the meaning of an effective diffusion coefficient.

In liquids, as is well known, the condition of strong narrowing is satisfied: the Larmor frequency is much smaller than the inverse correlation time. In this case the relaxation times are expressed only through the Fourier transform of the correlation function corresponding to zero frequency ([1],[2]). Consequently, under the conditions of strong narrowing we shall need only the value $d(0)$. At $p = 0$ the integral over dy in (6) is the discontinuous Weber-Schafheitlin integral ([9]), and

$$\widetilde{W}_m(\mathbf{r}, 0) = \frac{Y_2^{m*}}{10d(0)}\Phi(r), \tag{8}$$

where

$$\Phi(r) = \frac{1}{r^3}\int_0^r x\rho_0^{1/2}(x)\,dx + r^2\int_r^\infty dx\,\frac{\rho_0^{1/2}(x)}{x^4}. \tag{9}$$

When substituting (8) into (6), it is convenient to use the formula for the gradient of spherical functions $^{(10)}$. As a result one obtains

$$d(0) = D\int_0^\infty dr\left[\varphi_1(r)\left(r^2\Phi'^2 + 6\Phi^2\right) - \frac{3r^2}{4}\Phi'^2\varphi_2(r)\right]\Big/ 5\int_0^\infty dr\,\frac{\rho_0^{1/2}(r)}{r}\Phi(r). \tag{10}$$

If one assumes that

$$\rho_0(r) = \begin{cases} 0, & r \le 2a, \\ N, & r > 2a, \end{cases} \tag{11}$$

then (10) gives

$$d(0) = 0.81D. \tag{12}$$

Thus, the hydrodynamic interaction leads to an effective decrease of the diffusion coefficient.

Substitution of (8) into the known expression for the spin-lattice relaxation time in a system of identical nuclei $^{(1,2)}$ gives that the intermolecular contribution, or, as it is often called, the contribution of translational molecular motion to spin-lattice relaxation, is equal to

$$\left(\frac{1}{T_1}\right)_{\text{trans}} = \frac{8I(I+1)\pi\gamma^4\hbar^2}{5d(0)}\int_0^\infty dr\,\frac{\rho_0^{1/2}(r)}{r}\Phi(r), \tag{13}$$

where I is the spin, and γ is the gyromagnetic ratio of the resonating nucleus. Relation (13) differs from the formula of Oppenheim and Bloom $^{(8)}$ only in the form of writing and by the replacement of D by $d(0)$. Consequently, allowance for the cooperativity of molecular motion leads to an increase in the intermolecular contribution to the relaxation times.

Relation (12) is valid only if the magnetic nuclei are located at the centers of the molecules. The case in which the magnetic nuclei are located on the periphery of the molecule was considered by Hubbard $^{(11)}$ on the basis of equation (1) and the assumption that, for D and the coefficient of rotational diffusion, the Stokes-Einstein formulas are valid and that the radial distribution function has the form (11). Hubbard found that the formula for the intermolecular contribution includes the correction factor

$$f = (1 + 0.233(b/a)^2 + 0.15(b/a)^4 + ...),$$

where b is the distance of the magnetic nucleus from the center of the molecule. Strictly speaking, if one takes the actual radial function and takes account of the hydrodynamic interaction, then the value of Hubbard' s correction factor will change. However, the approximate character of our calculation makes the introduction of corrections to Hubbard' s correction poorly justified. Therefore, in the case of "noncentral" magnetic nuclei, we shall introduce Hubbard' s correction into formula (12) in unchanged form.

By tradition, theories of magnetic relaxation in liquids are compared with experimental data for water. Recently Krinitskii (12) carried out measurements of T_1 in carefully purified water. The radial distribution function for water at 28°C was measured by Brady and Romanov (13). Values of D were measured, in particular, by Simpson and Carr (14). They obtained that at 30°C, $D = 2.46 \cdot 10^{-5}$ cm^2/s. If, for Hubbard' s correction, one takes the value calculated by Krinitskii (12), then without allowance for the hydrodynamic interaction $(1/T_1)_{\text{trans}}$ at 30°C will be 0.096 s^{-1}. With allowance for the hydrodynamic interaction,

$$(1/T_1)_{\text{trans}} = 0.119 \text{ s}^{-1}.$$

The contribution of rotational molecular motion (the intramolecular contribution) to the relaxation is determined by the rotational correlation time τ_c (1,2). The time τ_c for water can be found from data on dielectric relaxa-

according to the Paul relation (15), obtained later by Glarum (16) by the method of correlation functions:

$$\tau_c = \tau_d(2\varepsilon_0 + \varepsilon_\infty)/9\varepsilon_0,$$

where τ_d is the dielectric relaxation time, and ε_0 and ε_∞ are the values of the dielectric constant at zero and infinitely high frequencies, respectively. From the data on dielectric relaxation in water (17) it follows that the intramolecular contribution to the relaxation at 30° is $(1/T_1)_{\text{in}} = 0.119$ sec^{-1}. Consequently, without taking hydrodynamic interaction into account one obtains $T_1 = 4.65$ sec, and with it taken into account $T_1 = 4.2$ sec. The experimental value of Krynicki (12) is $T_1 = 4.03$ sec. If the value of D quoted by Krynicki is used, the corresponding values obtained are 4.56 and 4.1 sec. Thus, even a very rough allowance for the cooperativity of molecular motion substantially improves the agreement of theory with experiment.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
16 XI 1966

REFERENCES

1. I. V. Aleksandrov, *Theory of Nuclear Magnetic Resonance*, Moscow, 1964, § 5.
2. A. Abragam, *Nuclear Magnetism*, Moscow, 1963, Ch. VIII.
3. N. Bloembergen, E. M. Purcell, R. V. Pound, Phys. Rev., **73**, No. 7, 679 (1948).
4. P. Gray, Mol. Phys., **7**, No. 3, 255 (1963–1964).
5. W. Ebeling, Ann. Phys. (DDR), **16**, Nos. 3–4, 147 (1965).
6. V. N. Tsvetkov, V. E. Eskin, S. Ya. Frenkel, *Structure of Macromolecules in Solutions*, Moscow, 1965.
7. V. M. Fain, ZhETF, **44**, No. 6, 1915 (1963).
8. I. Oppenheim, M. Bloom, Canad. J. Phys., **39**, No. 6, 845 (1961).
9. G. N. Watson, *A Treatise on the Theory of Bessel Functions*, Part 1, Moscow, 1949, p. 439.
10. M. E. Rose, *Elementary Theory of Angular Momentum*, N. Y.–London, 1957, p. 120.
11. P. S. Hubbard, Phys. Rev., **131**, No. 1, 275 (1963).
12. K. Krynicki, Physica, **32**, No. 1, 167 (1966).
13. G. W. Brady, J. J. Romanow, J. Chem. Phys., **32**, No. 1, 306 (1960).
14. S. H. Simpson, H. Y. Carr, Phys. Rev., **111**, No. 5, 1201 (1958).
15. I. G. Powles, J. Chem. Phys., **21**, No. 4, 633 (1953).
16. S. H. Glarum, J. Chem. Phys., **33**, No. 5, 1371 (1960).
17. C. H. Collie, J. B. Hasted, D. M. Ritson, Proc. Phys. Soc. (London), **60**, 145 (1948).

Note: Figure translations are in progress. See original paper for figures.