INTERMOLECULAR NUCLEAR RELAXATIONS AND MOLECULAR SITE-SITE PAIR CORRELATION FUNCTIONS IN LIQUIDS

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Intermolecular nuclear relaxation studies of real liquids and the results of theoretical calculations for model potential functions have provided significant information on the role of molecular interactions in the structure of liquids. The intermolecular proton-proton paircorrelation function (pcf), obtained from the reference interaction site model (RISM) is used as the equilibrium distribution and is used to obtarn an effective force for the calculation of intermolecular proton relaxation rates in liquid benzene, 1,3,5-trideuterobenzene and ethane. For liquid ethane, better agreement with experiment is observed with the pcf obtained from the Monte Carlo simulation than with the RISM result.

The intermolecular nuclear spin relaxation in liquids is due to the dipole-dipole interaction modulated by the diffusion processes of spin bearing molecules. This process is usually described by the Smoluchowski model[1]. Considering the relative diffusion between the spin bearing molecules, Abragm[1] utilized an independent diffussion model and allowed penetrable diffusion on the diffusion trajectory. However at the beginning and also at the end of the relative diffusion processes between the spin bearing molecules, penetration is not allowed within a distance of closest approach. Moreover, theoretical treatments of intermolecular relaxation are usually restricted to monoatomic liquids since the interacting nuclei are assumed to be at the centers of the spin bearing molecules. The correction of the offcenter effect of the spin site in a molecule has been considered by Hubbard[2]. The effects of the equilibrium distribution of molecules in the liquid were usually neglected. A useful description of the microscopic structure of a monoatomic liquid is the pair correlation function (pcf), $g(r)$, which gives the probability density of finding an atom at a distance r from another atom at the origin. Hwang and Freed[3] have considered the proper boundary condition under which the molecular spheres do not penetrate each other during the course of a trajectory. They also have shown how to correct the time-correlation functions and spectral densities needed for spin relaxation by including (atom) pair-correlation effects in the dynamic time-evolution of translational diffusion.

In a molecular liquid there exists a set of partial atom pair correlation functions, $g_{ij}(r)$, each of which describes the correlations of a distinct pair of atoms i, j constituting the molecule. Important contributions to the understanding of the equilibrium properties of molecular liquids have come from theoretical studies such

* The author, a professor of Chemistry at the National Taiwan University and formerly a chemistry student of the National Taiwan University from 1959 to 1963, wishes to dedicate this paper to Dr. Chien.

as the RISM equation[4] and Monte Carlo simulation[5]. The RISM theory assumes that the equilibrium distributions between molecules in a dense fluid are determined primarily by the short-range harshly repulsive portions of the intermolecular potential. These repulsive interactions are modeled as hard core interactions by assuming molecules are composed of overlapping hard spheres which are rigidly fused together. As a result, the model hard core interactions depend on the molecular orientation. The site-site pcf's are solved from the RISM integral equation. The agreement between the RISM theory and the results of neutron diffraction experiments, obtained without adjustable parameters, indicates that to a good approximation the local structure of liquids is determined by packing or steric effects. The pcf may also be obtained from a Monte Carlo simulation of liquids with a known molecular model and intermolecular interaction[5]. The validity of the pcf may be checked with the thermodynamic coefficients. However, the dependence of measurable thermodynamic coefficients upon the pair correlation function is of a long range nature. Thermodynamic measurements therefore are not very sensitive to the region where the intermolecular site-site interaction is effective. Also it is difficult to study the effect of molecular site-site correlation, because the thermodynamic coefficient is obtained in some average form of all site-site pcf's. To get more definite information about the intermolecular interactions one must turn to a comparison of non-thermodynamic coefficients measured on real systems and calculated from pair correlation function for model systems. The use of intermolecular spin relaxation rates is particularly suitable for this purpose since the perturbation due to dipolar interaction is of short range and only the specified site-site pcf is involved.

Recently, Zeidler[6] described intermolecular nuclear relaxation by including a molecular pcf in which both radial and orientational corrections were taken into account in the initial equilibrium distribution. For the dynamical process the independent diffusion model was still assumed. Hwang[7] used the site-site pcf from RISM calculations in his study of intermolecular proton relaxation processes in liquid acetonitrile, chloroform and ethane and obtained good agreement with experimental results. The utilization of the site-site pcf implicitly contains the correction for off-center effects. Furthermore, in liquid ethane and acetonitrile, invoking a uniform pcf gave 3 and 5 per cent enhancements in the respective relaxation rates in comparison with those obtained by using RISM pcf's, while in liquid chloroform the enhancement reached 22 per cent.

The purpose of this paper is to further evaluate proton relaxation rates by applying RISM results to liquid benzene and 1, 3, 5-trideuterated benzene. The comparison of proton relaxation rates for liquid ethane with pcf's calculated from the RISM and Monte Carlo method will be made.

THEORY

The contribution of intermolecular spin dipolar interactions to the NMR relaxation of identical nuclei may be obtained from the expression[1]

$$1/T_1=(4\pi/5)\gamma_H^4\hbar^2I(I+1)[J(\omega)+4J(2\omega)] \quad (1)$$

where γ_H is the gyromagnetic ratio of the proton and $I=1/2$ is the proton spin quantum number $J(\omega)$ is the spectral density, at Larmor precession frequency ω, defined by[1,2]

$$J(\omega)=2\,\mathrm{Re}\int_0^\infty \exp(i\omega t)G(t)dt, \quad (2)$$

where $G(t)$ is the time-correlation function for dipolar interaction between spins 1 and 2,

$$G(t)=(5/4\pi)n_H\int d^3r_0\int d^3r\, D^{*2}_{0,m}(\Omega_0) \cdot D^2_{0,m}(\Omega)p(r_0|r,t)g(r_0)/(r_0^3r^3). \quad (3)$$

In Eqs. (1) and (2), n_H is the average number density of proton spins. The function $p(r_0|r,t)$ is the conditional probability for the relative diffusion of spins 1 and 2, that is, given spins separated by r_0 at $t=0$, it gives the probability they are separated by r at time t. Also, $D^L_{n,m}(\Omega)$ is the Wigner rotation matrix element, depending on the sets of Eulerian angles Ω_0 and Ω at times zero and t which fix the coordinate system between the intermolecular vector r and the laboratory coordinate frame. We now approximate $p(r_0|r,t)$ by the solution of the Smoluchowski equation,

$$\frac{\partial p(r_0|r,t)}{\partial t}=D\nabla\cdot[\nabla p(r_0|r,t)+\nabla u(r)p(r_0|r,t)/kT] \quad (4)$$

with the initial condition

$$\lim_{t\to 0} p(r_0|r,t)=\delta(r-r_0). \quad (5)$$

Further boundary conditions are imposed for impenetrable diffusion

$$\left.\frac{\partial p(r_0|r,t)}{\partial r}\right|_{r=d}=0 \quad (6)$$

and at infinite separation

$$\lim_{r\to\infty} p(r_0|r,t)=0 \quad (7)$$

where d is the distance of closest approach between the intermolecular spin sites and taken to be the van-der-Waals diameter of the protons. In Eq. (4), D is the mutual diffusion coefficient and is assumed to equal to twice the self diffusion coefficient of the spin bearing molecule. Also, $u(r)$ is the potential of the averaged forces between the spin-bearing molecules and assumed for simplicity to depend only on the radial separation and not the molecular orientations. We may then obtain $u(r)$ from the pcf $g(r)$,

$$\ln g(r)=-u(r)/kT \quad (8)$$

so that one has an effective force

$$F(r)=-(\nabla u(r))/kT=\nabla(\ln g(r)). \quad (9)$$

The expression of Eq. (9) when incorporated into Eq. (4) means that in the limit $t\to\infty$, $p(r_0|r,t)$ will yield the equilibrium $g(r)$, while, for finite times, $F(r)$ is the driving force acting to restore this equilibrium. Here we treat $g(r)$ as the proton-proton pcf obtained from RISM calculations.

Eqs. (2) and (3) may be evaluated by means of the 3-point finite different method to solve the Smoluchowski equation, *e.g.*,

$$\frac{\partial f(r)}{\partial r}\longrightarrow\frac{f(r+\Delta r)-f(r-\Delta r)}{2\Delta r} \quad (10)$$

and

$$\frac{\partial^2 f(r)}{\partial r^2}\longrightarrow\frac{f(r+\Delta r)-2f(r)+f(r-\Delta r)}{(\Delta r)^2}. \quad (11)$$

The detailed numerical method is discussed elsewhere[3] and will not be given here.

RESULTS AND DISSCUSSION

The RISM integral equation is solved for the liquid models of benzene, 1, 3, 5-trideuterobenzene and ethane using Lowden's FORTRAN program[4]. The van der Waals diameter of the protons and deuterium, σ_H, is taken to be 2.4 Å[9] for all the RISM molecules given below. The RISM equation provides an approximate method for calculating atom-atom intermolecular pcf's including the proton-proton pcf needed in the calculation of relaxation rates.

Liquid benzene

The RISM picture of the benzene molecule is shown in Fig. 1. The molecule is assumed to be rigid. Lowden and Chandler[10] used reasonable values of the RISM parameters to determine X-ray scattering structure factors. They determined $\sigma_C=3.37$ Å as the van der Waals diameter for the carbon atoms. The $C-C$ bond length was taken as 1.40 Å and the $C-H$ bond length as 1.08 Å[10]. In addition, the following intramolecular atom-atom lengths[10] were used in the RISM calculations,

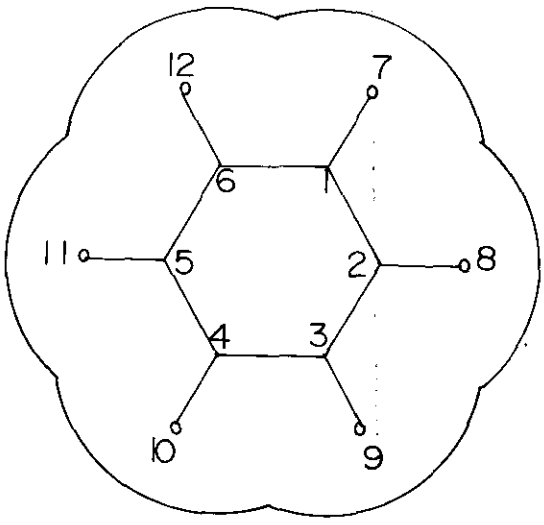

Fig. 1. The RISM model for benzene. Atoms 1 to 6 are carbons, 7 to 12 are hydrogens. The model parameters are given in the text.

$$\left.\begin{aligned} L_{7,8} &= 2.48\ \text{Å}, \\ L_{1,3} &= 2.42\ \text{Å}, \\ L_{1,4} &= 2.79\ \text{Å}, \\ L_{1,8} &= 2.15\ \text{Å}, \\ L_{3,7} &= 3.40\ \text{Å}, \\ L_{4,7} &= 3.87\ \text{Å}, \\ L_{7,9} &= 4.29\ \text{Å}, \\ L_{7,10} &= 4.95\ \text{Å} \end{aligned}\right\} \qquad (12)$$

The other distances can be obtained in accordance with the geometrical symmetry of the molecule. The molecular density of the liquid was taken to be $\rho = 6.759 \times 10^{-3}$ Å^{-3} at 25°. The proton-proton pcf obtained is shown in Fig. 2. Using the experimental self diffusion coefficient $D_s = 2.21 \times 10^{-5}$ $cm^2 s^{-1}$ [11], the calculated longitudinal relaxation rate at 25° and 60 *MHz* is $5.3 \times 10^{-2}\ s^{-1}$, a result that is about 30 per cent higher than the observed value ($3.8 \times 10^{-2}\ s^{-1}$)[12].

Narten[13] analyzed X-ray diffraction data for liquid benzene at 25° by using scattering factors for the $C-H$ groups rather than for individual C and H atoms. The data were used to find the RISM parameters of liquid benzene which then

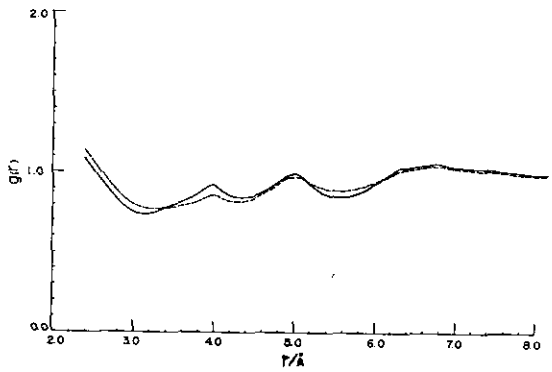

Fig. 2. Intermolecular proton-proton pair-correlation functions for liquid benzene and 1, 3, 5-trideuterobenzene. These functions were determined by solving the RISM equation with the molecular parameters given in the text. The dashed curve is for 1,3,5-trideuterobenzene, and the solid curve for benzene.

permit a calculation of the site-site pcf. Instead of the $\sigma_H = 2.4$ Å used here, $\sigma_H = 2.6$ Å was obtained from the best fit of the diffraction experiments. Analogous calculations were then made for the pcf's of the RISM. The calculated longitudinal relaxation rate yields $4.8 \times 10^{-2}\ s^{-1}$ which gives better agreement with experiment than that calculated with $\sigma_H = 2.4$ Å.

Liquid 1, 3, 5-trideuterobenzene

The parameters used in the RISM calculation for 1, 3, 5-trideuterobenzene are identical with those for benzene. The proton-proton pcf obtained is negligibly different from the one obtained for benzene as depicted in Fig. 2. Thus, the calculated longitudinal relaxation rate at 25° and 60 *MHz* is $2.7 \times 10^{-2}\ s^{-1}$ about one half of the value for liquid benzene. The experimental value under the same conditions is $1.9 \times 10^{-2}\ s^{-1}$ [14].

Liquid Ethane

Byrnes and Sandler[15] applied Monte Carlo simulation to liquid ethane. Their results show the lack of importance of intramolecular rotation in liquids. Thus,

the structure of ethane molecules in the liquid state may be considered only slightly perturbed from the staggered conformation. The staggered conformer of ethane is therefore used in the RISM calculation.

The RISM equation is solved for liquid ethane with the conformation parameters given in ref[7]. and with a molecular density $\rho=0.0126\,Å^{-3}$ at $105\,K$. The resulting proton-proton pcf is shown in figure 3. Byrnes and Sandler's result of Monte Carlo simulations of liquid ethane at $105\,K$ is presented also. Their simulation is based on an eight-site model of ethane with staggered conformation. The Williams VII potential is invoked for interacting sites with parameters calculated from experimental data. In Fig. 3, it is found that at short intermolecular distance the RISM result has a larger value than the Monte Carlo reault. This may be interpreted by the fact that the hard core potential is used in the RISM calculation while the exponential repulsion potential is used in the Monte Carlo simulation. By taking advantage of the experimental self diffusion coefficient $D_s=0.94\times10^{-5}\,cm^2s^{-1}$ at $105\,K$[15], the calculated relaxation rate $1/T_1$ at a Larmor frequency of $30\,MHz$ gives

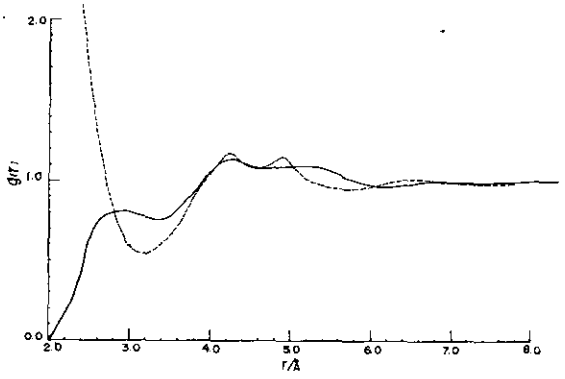

Fig. 3. Intermolecular proton-proton pair correlation functions for liquid ethane at $105\,K$ with molecular density $\rho=0.0126\,Å^{-3}$. The dashed curve is obtained from the RISM calculation, and the solid curve from the Monte Carlo calculation of Byrnes and Sandler.

$0.26\,s^{-1}$ for the pcf derived from the RISM calculation. In order to have a convergent computation, we made a cut-off at $r=2.1$ Å for calculation with the Monte Carlo pcf. The calculated $1/T_1$ yields $0.24\,s^{-1}$. If we extend the cut-off distance to 2.4 Å, it only shows a 4 per cent decrease in the relaxation rate. The results are in good agreement with the observed value $(0.23\,s^{-1})$[15].

CONCLUSION

Intermolecular NMR relaxation may be utilized to determine the molecular potential used in the calculation of pcf's, since NMR relaxation rates are sensitive to the details of the interaction at short range. In particular, no other physical method is suitable for checking the reliability of the site-site pcf's The agreement of relaxation rates from RISM and Monte Carlo calculations with experiment indicates that the results of these two methods are good approximations to represent the equilibrium properties of the liquids. Better agreement from the Monte Carlo result, found for liquid ethane at $105\,K$, shows that at short intermolecular distances a soft core repulsive potential is a better model than the hard core potential. It is concluded that relaxation rates such as those studied here will be useful for selecting models to represent the intermolecular interactions in liquids.

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