

Dynamic effects of pair correlation functions on spin relaxation by translational diffusion in two-dimensional fluids

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The dynamic effects of pair correlation functions (pcf) on spin relaxation by translational diffusion in *infinite* two-dimensional fluids are considered explicitly through a Smoluchowski equation, for the usual conditional probability, with appropriate boundary conditions, especially at the contact separation of the interacting pair of molecules. The solution of this equation by finite difference techniques permits the calculation of time correlation functions, spectral densities, and spin-relaxation rates associated with a dipolar relaxation mechanism between the spin-bearing molecules. Comparison of the two-dimensional spin-relaxation results obtained with different pcf is presented. The spectral densities and spin-relaxation rates are indeed found to be significantly altered by the pcf. For example, for a nonuniform pcf, the two-dimensional spectral densities, at (and above) the Larmor frequency ω_0 , are greater for translational correlation times τ_t that are an order of magnitude faster than $\tau_t = \omega_0^{-1}$ which provides the maximum spectral density in bulk theory. This *fast motion* result is consistent with the two-dimensional dynamical results found by other techniques. Moreover for a nonuniform pcf and a *single* translational correlation time, *two* well-defined minima are found in the variation of the spin-lattice relaxation time with the diffusion coefficient. This could be very useful for interpreting the spin-relaxation data of diffusing complexes in clays, intercalation compounds, and bilayers.

I. INTRODUCTION

The usual theories of spin relaxation by translational molecular diffusion whether for three-dimensional^{1,2} or two-dimensional^{3,4} systems do not properly include the pair correlation function (pcf) into the dynamical description of the spin-bearing molecules. Hwang and Freed⁵ have included the radial pcf in the molecular dynamics through a Smoluchowski equation for the usual conditional probability with appropriate boundary conditions, especially at the contact separation of the interacting pair of molecules. They have solved such an equation by finite-difference techniques and have shown a significant enhancement of dipolar correlation functions and spectral densities for bulk liquids in comparison with previous treatments.

For two-dimensional systems, inclusion of the pcf in the spin-relaxation calculations becomes absolutely necessary owing to the additional steric hindrance that the interacting molecules pose to their diffusive motions at short intermolecular distance and the enhanced reencounter probabilities which drastically increase the effective period of interaction. In order to take account of such a pcf in two-dimensional

planar systems we apply, in this paper, the method of Hwang and Freed for bulk liquids. This enables us to calculate the dipolar correlation functions and spectral densities for uniform and nonuniform pcf. The spectral densities and spin-relaxation rates are indeed found to be significantly altered by the pcf. For example, for nonuniform pcf, the two-dimensional reduced spectral density at and above the Larmor frequency ω_0 is greater for translational correlation times $\tau_t = 0.1/\omega_0$ than for $\tau_t = 1/\omega_0$ contrary to the usual three-dimensional results. This is consistent with the interpretation given in a previous work on spin relaxation and quasi-elastic neutron scattering of heterogeneous systems physisorbed on solid surfaces.⁶ Moreover, at high frequency, i.e., ($\geq \omega_0$), such a two-dimensional spectral density spreads effectively over a larger band for fast motions than for slow motions, which is just the opposite of the three-dimensional case. Another consequence is that the low frequency logarithmic divergence predicted in previous works^{3(a)-3(d)} is now found to be significantly reduced in importance. Finally, we present the theoretical variation of the spin-lattice relaxation time with the translational diffusion coefficient D , for different orientations β of the normal to the plane of diffusion relative to the constant magnetic field, in cases of both uniform and nonuniform pcf. The presence of a highly nonuniform pcf for $\beta = \pi/2$ induces *two* pronounced minima in these variations, with a *single* translational correlation time, which could explain the magnetic resonance observa-

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tions of diffusing complexes in solid electrolytes⁷ and intercalation compounds.⁸

II. DIPOLAR RELAXATION IN INFINITE TWO-DIMENSIONAL SYSTEMS

In infinite two-dimensional spin systems the anisotropic pairwise dipolar autocorrelation functions $G^{(q)}(\tau)$ ($q \in \{0, 1, 2\}$), which describe the persistence of the fluctuating dipolar energy modulated by the two-dimensional diffusion of the spin-bearing molecules, and the spectral densities $J^{(q)}(\omega)$, can be expressed as

$$G^{(q)}(\tau) = n_I \int d^2 \rho_0 \int d^2 \rho E_L^{(q)}(0) \times P(\rho, \tau | \rho_0, 0) g(\rho_0) E_L^{(q)*}(\tau), \quad (1a)$$

$$J^{(q)}(\omega) = 2 \operatorname{Re} \int_0^\infty e^{i\omega\tau} G^{(q)}(\tau) d\tau, \quad (1b)$$

where n_I is the number of spins I per unit area, and P is the usual conditional probability whose form depends on the model chosen for the molecular dynamics. The $E_L^{(q)}(\tau)$ are the fluctuating dipolar terms expressed in the laboratory frame L with a \mathbf{z}_L axis parallel to the applied constant magnetic field \mathbf{B}_0 . These terms can be conveniently expressed in the planar fixed axis system M where the \mathbf{z}_M axis is parallel to the normal \mathbf{n} to the planar surface

$$E_L^{(q)}(\tau) = \sum_{m=0, \pm 2} E_M^{(m)}(\tau) d_{mq}^{(2)}(\beta), \quad q \in \{-2, 2\}, \quad (2)$$

where

$$E_M^{(0)}(\tau) = \alpha_0 \gamma_I^2 \hbar^2 \rho(\tau)^{-3}, \quad E_M^{(\pm 1)}(\tau) = 0, \quad (3)$$

$$E_M^{(\pm 2)}(\tau) = -\alpha_2 \gamma_I^2 \hbar^2 \rho(\tau)^{-3} e^{-\epsilon 2i\varphi(\tau)},$$

with $\epsilon \equiv \pm 1$, $\alpha_0 = 1/2\sqrt{3/2}$, and $\alpha_2 = 3/4$. Here (ρ, φ) are the cylindrical coordinates in the M axis system of the vector ρ between the two interacting spins, and $d_{mq}^{(2)}(\beta)$ are the well-known Wigner rotation coefficients.⁹

In order to represent the dynamics of the interacting molecules we use a Smoluchowski equation.¹⁰ This implies the well-known restriction that the oscillatory-type behavior due to the motion in the presence of short range intermolecular forces is overdamped. Then the molecular dynamics is properly described for times long compared to the inverse of the friction coefficient. It would be possible, in principle to include such oscillatory type behavior through a generalized Langevin equation^{11,12} or by a generalized Smoluchowski equation.¹³

Within the framework of the Smoluchowski equation we consider the molecular motions relative to an average force field due to the intermolecular interactions. Assuming that the two interacting molecules have similar size and mass and that the average force $\mathbf{F}(\rho)$ between them is related to an effective radial potential $U(\rho)$ and a radial pcf $g(\rho)$:

$$\mathbf{F}(\rho) \equiv -\nabla U(\rho) = kT \nabla \ln g(\rho), \quad (4)$$

one thus approximates P , in Eq. (1), as the solution of a Smoluchowski equation given in cylindrical polar coordinates by

$$\frac{\partial P(\rho, \tau | \rho_0, 0)}{\partial \tau} = D [\Gamma_\rho + \Gamma_\varphi / \rho^2] P(\rho, \tau | \rho_0, 0), \quad (5)$$

with the initial condition

$$\lim_{\tau \rightarrow 0} P(\rho, \tau | \rho_0, 0) = \delta(\rho - \rho_0). \quad (6a)$$

This Smoluchowski equation has the property that

$$\lim_{\tau \rightarrow \infty} P(\rho, \tau | \rho_0, 0) = g(\rho_0). \quad (6b)$$

In Eq. (5) $D = D_1 + D_2$ is the coefficient for the relative translational diffusion and the radial Γ_ρ , and orientational Γ_φ operators are given, respectively, by

$$\Gamma_\rho P(\rho, \tau | \rho_0, 0) = \rho^{-1} \frac{\partial}{\partial \rho} \left\{ \rho \frac{\partial}{\partial \rho} P(\rho, \tau | \rho_0, 0) - \rho |\mathbf{F}(\rho)| / kT P(\rho, \tau | \rho_0, 0) \right\}, \quad (7a)$$

$$\Gamma_\varphi P(\rho, \tau | \rho_0, 0) = \frac{\partial^2}{\partial \varphi^2} P(\rho, \tau | \rho_0, 0). \quad (7b)$$

An application to two-dimensional systems of the same procedure proposed by Hwang and Freed⁵ for bulk liquids leads, after some algebraic manipulations using Eqs. (1b)–(7b), to the following spectral density given in operator form as

$$J^{(q)}(\beta, \omega) = 4\pi n_I \gamma_I^4 \hbar^4 \operatorname{Re} \sum_{m=0, \pm 2} |d_{mq}^{(2)}(\beta)|^2 \alpha_m^2 \times \int_d^\infty \rho^{-2} d\rho \{ -D [\Gamma_\rho - m^2 / \rho^2] - i\omega \}^{-1} \rho^{-3} g(\rho), \quad (8)$$

where α_m is given in Eq. (3). The action of the operator in brackets in Eq. (8) can be evaluated in matrix form using the finite difference technique. This implies giving discrete values for the intermolecular distances ρ_i starting from the distance of minimal approach, $\rho_0 \equiv d$, to the assumed maximal distance ρ_N , according to: $\rho_{i+1} = \rho_i + \Delta\rho_i$ for $i \in \{0, \dots, N\}$ where the relative increments $\Delta\rho_i$ satisfy $\Delta\rho_i / d \ll 1$. Different possibilities exist for such discretization. Due to the presence of large amplitude oscillations in $g(\rho_i)$ for values of ρ_i up to a few times the distance of minimal approach d (Fig. 1), we distinguish the ρ space according to the two following regions: (i) The region $d \leq \rho_i \leq \rho_M$, where $g(\rho_i) \neq 1$; (ii) the region $\rho_M < \rho_i \leq \rho_N$ where $g(\rho_i) = 1$ and $F(\rho_i) = 0$. With such a grid, one can transform the differential operator Γ_ρ , defined in Eq. (7a), as a finite difference operator and the integral over ρ as a summation over the index i . Introducing now the dimensionless variables:

$$y_i \equiv \rho_i / d, \quad \Delta y_i \equiv \Delta\rho_i / d, \quad f(i) \equiv dF(i) / kT, \quad (9)$$

one can write Eq. (8) in a matrix form as

$$J^{(q)}(\beta, \omega) = 4\pi n_I \gamma_I^4 \hbar^4 \sum_{m=0, \pm 2} |d_{mq}^{(2)}(\beta)|^2 \alpha_m^2 \times (-\tau_i / d^4) \sum_{i=0, N} \Delta y_i / y_i^2 \{ \mathbb{W}^{(m)2} + \omega^2 \tau_i^2 \mathbf{1} \}^{-1} \mathbb{W}^{(m)} \{ g(y_i) / y_i^3 \}. \quad (10)$$

In this equation $\tau_i = d^2 / D$ is the translational correlation time, $\mathbf{1}$ is the diagonal (N, N) unit matrix, $\{g(y_i) / y_i^3\}$ is a

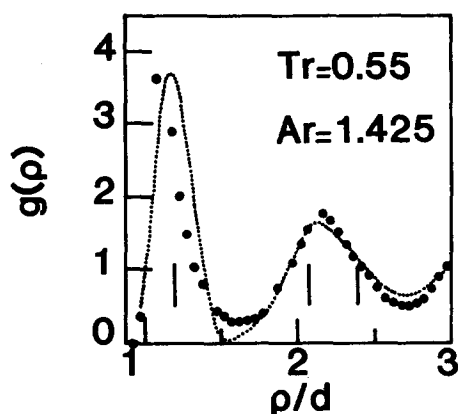


FIG. 1. Comparison of the pcf, $g(\rho)$ (dotted line), described in the text with the Monte Carlo computation of a two-dimensional system of particles interacting with a Lennard-Jones potential (points from Ref. 17). The bold vertical marks indicate the position of the first three shells of neighbors in a perfect hexagonal lattice at the same reduced density A_r . $T_r = kT/\epsilon$ is a dimensionless parameter which simulates the ratio of kinetic energy over the maximum value ϵ of the harmonic potential of the particles relative to their average position in each site.

$(N, 1)$ column vector, and $\mathbb{W}^{(m)}$ is the tridiagonal “transition probability” (N, N) matrix between discrete values of ρ_i previously introduced by Pedersen and Freed¹⁴ for three dimensions and Zientara and Freed for two dimensions,¹⁵ whose dimensionless elements are given in Table I.

We have chosen for the elements given in Table I: $\Delta y = 0.025$, $y_M \sim 6$, $y_N \sim 60$ which gives $N \sim 2500$ for the size of the matrix \mathbb{W} . This value for the unique increment Δy of the grid gives a sufficient precision on the pcf in its highly oscillating region limited by y_M . Thus a criteria of convergence for the numerical summation, given in Eq. (10), is that one notes no variation when decreasing Δy for a given y_N . The choice of the quasi-infinite size of the grid $y_N \sim 60$ is arbitrary and corresponds to an intermolecular distance for which the calculated value of Eq. (10), for a given frequency ($\neq 0$), does not vary when increasing y_N . However, there is a slight sensitivity of Eq. (10) to the maximal size of the grid (y_N) at zero frequency. The presence of an outer absorbing boundary condition for the translational part of the last diagonal elements, $\mathbb{W}_{N,N} = 0$ in Table I, greatly reduces this size

TABLE I. Transition-probability tridiagonal matrix elements.

$\mathbb{W}_{0,0}^{(m)} = -[2/\Delta y^2 + y_1 f(1)/\Delta y] - m^2$	$j = 0$
$\mathbb{W}_{0,1}^{(m)} = [2/\Delta y^2 - f(0)/\Delta y]$	
with $\Delta y_0 = \Delta y/2$	
$\mathbb{W}_{j,j\pm 1}^{(m)} = \{1/\Delta y^2 \pm [2y_j \Delta y]^{-1} [1 - y_j f(j)]\}$	$0 < j < N$
$\mathbb{W}_{j,j}^{(m)} = -\{2/\Delta y^2 + [2y_j \Delta y]^{-1} [y_{j+1} f(j+1) - y_{j-1} f(j-1)] + (m/y_j)^2\}$	
with $\Delta y_j = \Delta y$ and $f(j) = 0$ for $j > M$,	
	$j = N$
$\mathbb{W}_{N,N-1}^{(m)} = 2/\Delta y^2$	
$\mathbb{W}_{N,N}^{(m)} = -(m/\Delta y)^2$	
$\mathbb{W}_{N-1,N}^{(m)} = 0$	
with $\Delta y_N = \Delta y/2$.	

dependence. The translational parts of these matrix elements (without the diagonal m^2 terms) are naturally required to satisfy the conservation of total probability given by the relation

$$\sum_{i=j-1, j, j+1} y_i \Delta y_i \mathbb{W}_{i,j}^{(m)} = 0, \quad j \in \{0, \dots, N\}, \quad (11)$$

which becomes equivalent to a reflecting-wall boundary condition at $\rho_0 = d$.

It is certainly more convenient to solve Eq. (10) by a single diagonalization instead of directly inverting the matrix for each frequency ω . For that we have used a method which transforms the matrix $\mathbb{W}^{(m)}$ into a symmetric and diagonal form $\mathbb{C}^{(m)}$ by a similarity transformation \mathbb{T}^5 :

$$\mathbb{C}^{(m)} = \mathbb{T} \mathbb{W}^{(m)} \mathbb{T}^{-1}. \quad (12)$$

Equation (10) then becomes

$$J^{(q)}(\beta, \omega) = 4\pi n_l \gamma_l^A \hbar^4 \sum_{m=0, \pm 2} |d_{mq}^{(2)}(\beta)|^2 \alpha_m^2 \times (-\tau_i/d^4) \sum_{i,j,k=0,N} \Delta y_i / y_i^2 T_{ij}^{-1} \{C_{ij}^{(m)} / [(C_{ij}^{(m)})^2 + \omega^2 \tau_i^2]\} T_{jk} g(y_k) / y_k^3. \quad (13)$$

And the well-known expressions for T_1^{-1} and T_2^{-1} are then²

$$T_1^{-1}(\beta) = 2/3 I(I+1) \hbar^{-2} [J^{(1)}(\beta, \omega_0) + 4J^{(2)}(\beta, 2\omega_0)], \quad (14)$$

$$T_2^{-1}(\beta) = I(I+1) \hbar^{-2} [J^{(0)}(\beta, 0) + 5/3 J^{(1)}(\beta, \omega_0) + 2/3 J^{(2)}(\beta, 2\omega_0)], \quad (15)$$

with the spectral densities given by Eq. (13).

III. DISCUSSIONS OF THE PAIR CORRELATION EFFECTS

In order to calculate the spectral densities given in Eq. (13), we need an expression for the pcf in two-dimensional fluids. Lado has proposed a numerical solution of the Percus–Yevick equation but only for two-dimensional hard disks.¹⁶ For a Lennard-Jones potential there are only Monte Carlo computations of the pcf, at various densities,¹⁷ which show a surprisingly “long range” local order close to the hexagonal packing (see the points in the Fig. 1). For that reason we have used a simple analytical expression for the pcf as a superposition of normalized Gaussians centered on the successive neighboring sites, from a reference molecule, in a perfect hexagonal lattice at the reduced density $A_r = (2/\sqrt{3})/(\sigma d^2)$ (by comparison with the closed packing density where $A_r = 1$), σ being the particle number density. In this expression the Gaussians are multiplied by the number of neighbors in each shell, and their widths are dependent on the degree of molecular mobility, which is assumed to increase progressively with the index of the shells. As shown in Fig. 1 our expression, which is normalized to one at long range ($\rho \gg d$), follows relatively close to the values obtained from the Monte Carlo pcf.¹⁷

In Figs. 2(a) and 2(b), we have displayed the time decays of the normalized dipolar correlation functions $G^{(0)}(\tau)/G^{(0)}(0)$ and the dispersion curves of the reduced spectral densities $j^{(0)}(\omega \tau_i)/\tau_i$ for $\beta = 0$ and three different cases of

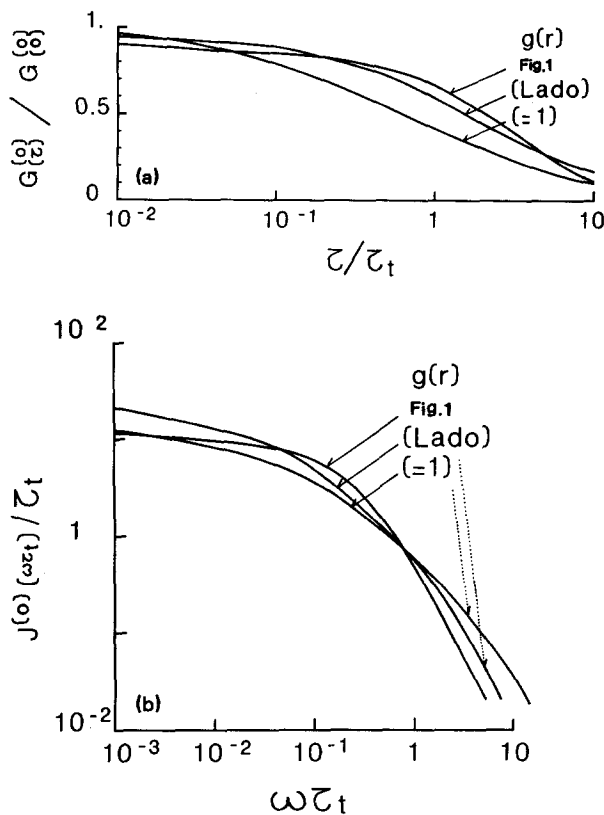


FIG. 2. (a) Semilogarithmic plots of the calculated variation of the normalized dipolar correlation functions $G^{(0)}(\tau)/G^{(0)}(0)$ vs τ/τ_t (where $\tau_t = d^2/D$) for $\beta = 0$ and different pcf, namely, (i) the pcf of Fig. 1; (ii) the Lado's pcf from Ref. 16; (iii) the uniform pcf. (b) Logarithmic plots of the calculated variation of the reduced spectral density $j^{(0)}(\omega\tau_t)/\tau_t$ vs $\omega\tau_t$ for $\beta = 0$ and the same pcf described in the legend of Fig. 2(a).

pcf. For the nonuniform pcf one has a longer persistence of the dipolar correlations at long time than obtained with the uniform pcf [Fig. 2(a)]. This is due to the additional steric hindrance that the interacting molecules pose to their diffusive motions at short intermolecular distance. This pair correlation effect persists even at long time owing to the enhancement of the reencounter probabilities in two dimensions¹⁸ which drastically increases the effective period of interaction. Corresponding to this the reduced spectral densities for the nonuniform pcf are increased at low frequency, i.e., $\omega\tau_t \leq 1$ [Fig. 2(b)]. This figure shows the sensitivity of our calculations to different models of pcf. For example, the significant differences observed between $j_{La}^{(0)}(\omega\tau_t)$ computed with the pcf of Ref. 16 and $j^{(0)}(\omega\tau_t)$ computed with the pcf of Fig. 1 (both calculated with the same reduced density A_r), are mainly due to the shift in the positions of the first maximum of the pcf in the two models. In Lado's work, restricted to the hard-disk approximation,¹⁶ this position corresponds to the distance of minimal approach $\rho = d$. In our calculations, which take into account the molecular interactions, this position corresponds to $\rho = d\sqrt{A_r}$, which is greater than d . Basically this has the effect of significantly enhancing the magnitude of $j_{La}^{(0)}(\omega\tau_t)$ at high frequency ($\omega\tau_t \geq 1$), since the most effective modes of relaxation in this frequency domain reflect the shorter range interactions at d .

On the other hand, one notes an enhancement of the magnitude of $j^{(0)}(\omega\tau_t)$ in a lower domain $0.1 \leq \omega\tau_t \leq 1$, since the shorter range interactions are now shifted at $d\sqrt{A_r}$. However, due to the reflecting-wall condition, $dP/d\rho|_{\rho=d} = 0$, all the different models of pcf give the same ω^{-2} dependence at a sufficiently high level of frequency.

To clearly separate the frequency ω and dynamical τ_t variables in the dispersion curves of $j^{(0)}(\omega\tau_t)$, either for a uniform or a nonuniform pcf, we have displayed in Figs. 3(a) and 3(b) the frequency dependence of $j^{(0)}(\nu)$ for two different values of τ_t , say $1/\omega_0$ and $0.1/\omega_0$ (ω_0 being the Larmor frequency characterized by a bold vertical arrow in the figures). The results for uniform three- and two-dimensional fluids, shown in Fig. 3(a), confirm the very large dimensionality effect especially at zero frequency where $j_{2D}^{(0)}(0)$ is greater than $j_{3D}^{(0)}(0)$ by at least two orders of magnitude. As is well known in bulk theory,^{1,2} $j_{3D}^{(0)}(\nu_0)$ is much greater for $\tau_t \sim 1/\omega_0$ than for $\tau_t \sim 0.1/\omega_0$. This is not the case for uniform two-dimensional fluids where these two $j_{2D}^{(0)}(\nu_0)$ values are of the same order of magnitude and the associated curves almost merge [Fig. 3(a)]. The same effect is evidenced for $j_{2D}^{(q)}(\nu_0)$ ($q = 1, 2$), thus indicating a very shallow minimum in the temperature variation of the spin lattice relaxation time T_1 . In presence of a nonuniform pcf [Fig. 3(b)], these two latter curves are well separated. Now $j_{2D}^{(0)}(\nu)$ at and above ν_0 is greater for $\tau_t \sim 0.1/\omega_0$ than for $\tau_t \sim 1/\omega_0$. This is consistent with the fast motion interpretation given in a previous work on proton NMR relaxation studies of heterogeneous systems physisorbed on solid surfaces.⁶

One important consequence of this pair correlation effect is to create well-defined minima in the variations of T_1 [Eq. (14)] with the diffusion coefficient D , as shown in Figs. 4(a) and 4(b). These variations are symmetrical around a single minimum for $\beta = 0$ [Fig. 4(a)], either for a uniform

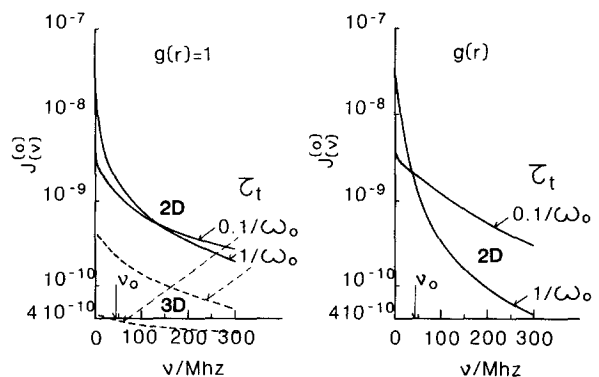


FIG. 3. (a) Semilogarithmic plots of the calculated variation of the reduced spectral density $J^{(0)}(\nu)$ vs ν (MHz) for a uniform pcf. The continuous lines correspond to the two-dimensional case for $\beta = 0$ and the dashed lines correspond to the three-dimensional case (from Ref. 19). In each case, we present the results for two values of τ_t , $1/\omega_0$ and $0.1/\omega_0$, with the chosen Larmor frequency ν_0 represented as a vertical arrow. (b) Semilogarithmic plots of the calculated variation of the reduced spectral density $J^{(0)}(\nu)$ vs ν (MHz) for the nonuniform pcf described in the text. The continuous lines correspond to the two-dimensional case for $\beta = 0$ and the same values of τ_t discussed above.

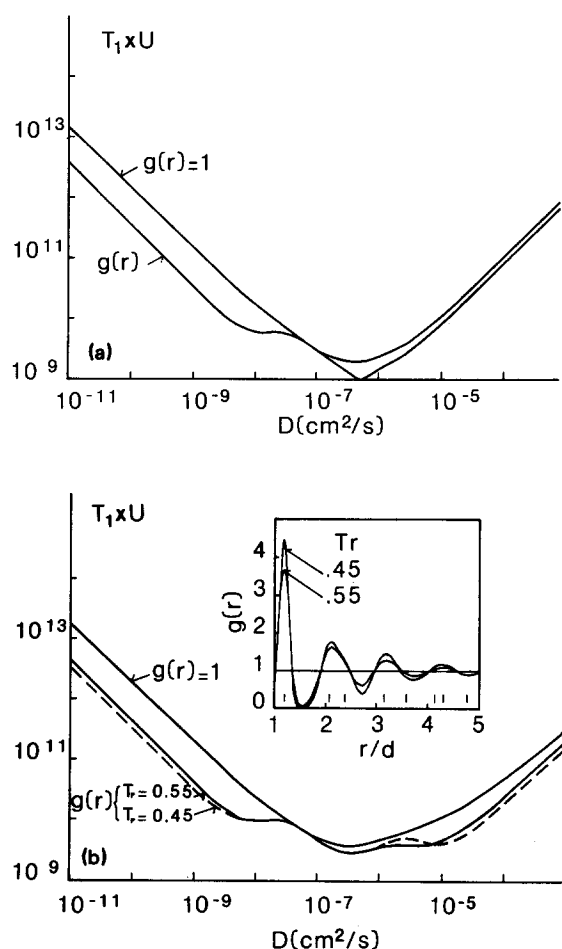


FIG. 4. Logarithmic plots of the calculated variation of the spin-lattice relaxation time T_1 ($\beta = 0$) vs D (cm^2/s) in the uniform and nonuniform (see Fig. 1) cases of pcf. Here $U = 6\pi\gamma^4\hbar^2 I(I+1)n_r d^{-4}$, $\nu_0 = 30$ MHz, $d = 6.5$ Å. (b) Logarithmic plots of the calculated variations of the spin-lattice relaxation time T_1 ($\beta = \pi/2$) vs D (cm^2/s) in the uniform and nonuniform cases of pcf. In the insert we see the influence of the T_r parameter, used in Fig. 1, on the amplitudes of oscillations of the pcf described in the text.

or a nonuniform pcf. This is different for $\beta = \pi/2$ [Fig. 4(b)] where these variations are highly unsymmetric around a single minimum, for $g(\rho) = 1$, and around two well-defined minima for $g(\rho) \neq 1$. These two minima become more and more pronounced when increasing the amplitude of the oscillations of $g(\rho)$, as shown in the insert of Fig. 4(b). The observation of *two minima* of T_1 with a *single* translational correlation time when one includes the pcf into the molecular dynamics is certainly the most striking result of this work. This could explain the proton relaxation studies of benzene in intercalation compounds in terms of a single translational correlation time of one type of molecule, instead of two, as it was considered in Ref. 8. This theory could also be useful in other infinite two-dimensional systems like the superionic conductors which present such wiggles in their temperature variations of T_1 .⁷

Finally we show, in Figs. 5(a) and 5(b), the anisotropies of the spin relaxation rates $T_1^{-1}(\beta)$ [Fig. 5(a)] and $T_2^{-1}(\beta)$ [Fig. 5(b)] for uniform and nonuniform pcf and fixed values of $\omega_0\tau_r$. Here again the pcf increases significant-

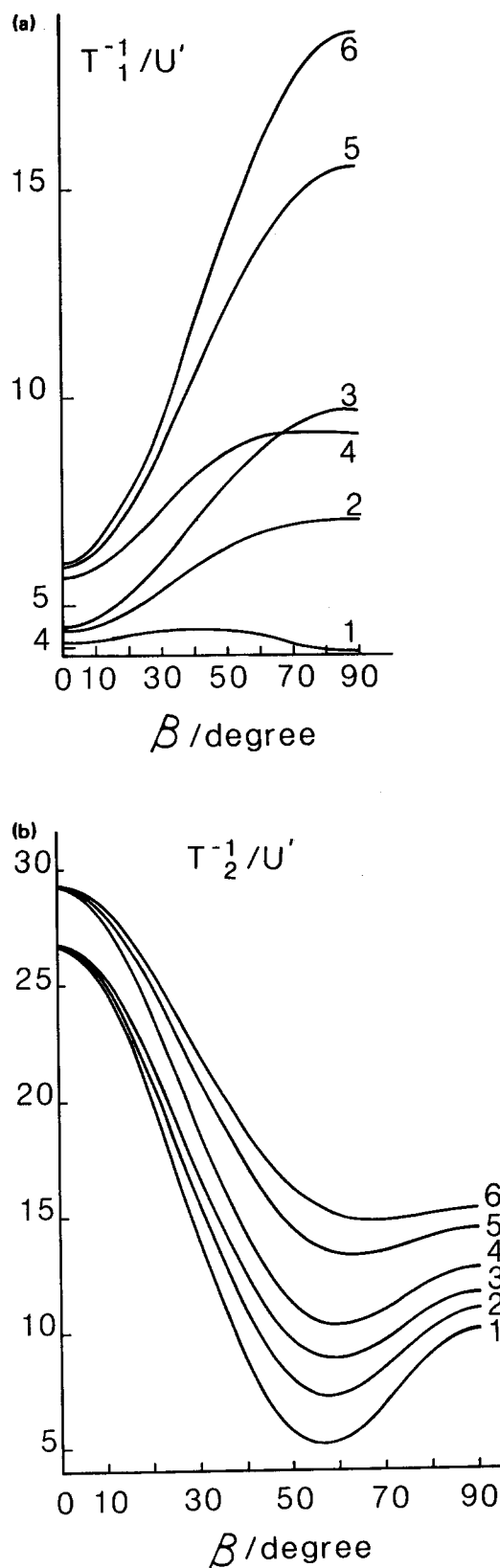


FIG. 5. (a) Angular variation of the spin-lattice relaxation rate T_1^{-1} vs β (degree). Here $U' = \{6\pi\gamma^4\hbar^2 I(I+1)n_r d^{-4}\tau_r\} \times 10^{11}$. The first three numbers (1-3) stand for the uniform pcf with the corresponding values of $\omega_0\tau_r$: 0.1, 0.03, 0.01, respectively. The last three numbers (4-6) stand for the nonuniform pcf described in the text with the following values of $\omega_0\tau_r$: 0.1, 0.03, 0.01, respectively. (b) Angular variations of the spin-spin relaxation rate T_2^{-1} vs β (deg). See the legend of Fig. 5(a) for the indices used in this figure.

ly the magnitude of these relaxation rates and profoundly alters their angular variations [see the curves 1 and 4 in Fig. 5(a)].

IV. CONCLUSION

We have studied the dynamic effects of pair correlation functions (pcf) on spin relaxation by translational diffusion in *infinite* two-dimensional fluids. This has been considered through a Smoluchowski equation with appropriate boundary conditions, especially at the contact separation of the interacting pair of molecules. Finite difference techniques have proven useful to solve this equation and to calculate the time correlation functions, the spectral densities, and the spin-relaxation rates associated with a dipolar relaxation mechanism between the spin-bearing molecules. Comparison of the relaxation results obtained with different pcf has been presented. The pcf alters significantly the variation of these relaxation results, with the frequency and the diffusion coefficient. For instance, in the presence of a nonuniform pcf and a single translational correlation time, two well-defined minima have been found in the variation of the spin-lattice relaxation time with the diffusion coefficient.

The method proposed could be useful for interpreting the relaxation experiments of diffusing complexes in clays, intercalation compounds, and bilayers.

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