

Dynamic effects of pair correlation functions on spin relaxation by translational diffusion in liquids. II. Finite jumps and independent T_1 processes

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Hwang and Freed have previously given solutions for the relative diffusion of molecules that include the proper boundary condition (i.e., an excluded volume due to a distance of minimum approach) which has usually been neglected in spin relaxation theories. In this work their results are extended to include effects of (1) one type of spin that is rapidly relaxing, (2) diffusion by jumps of finite size, and (3) frequency-dependent diffusion coefficients in the theory of spin relaxation by intermolecular dipolar interactions. These results are mathematically simpler and sounder than those commonly employed.

Hwang and Freed (HF) have shown in I¹ how to correct the time correlation functions and spectral densities needed for spin relaxation by translational diffusion by including the effects of the equilibrium pair-correlation function (pcf) between the spin-bearing molecules as an effective force in the relative diffusion equation. They showed that even a simple hard sphere model (applied to liquid ethane) could lead to an enhanced T_1^{-1} and to agreement with the Harmon-Muller (HM) experiment² without the need to introduce the Torrey³ theory for finite jumps. Also, much larger corrections were found by HF for $J(\omega)$ (the spectral density) at high frequencies ω , and even for $J(0)$ in the cases where the molecules can interact (e.g., shielded ionic interactions). These results, which include various pcf's, were obtained by numerical finite-difference methods described by HF.

It was also pointed out by HF that the approach previously used by other workers²⁻⁶ has neglected the boundary value problem which arises from a distance of closest approach d in the solution of the relative diffusion equation. [Only at a later stage in computing $J(\omega)$ are the contributions from $r < d$ ignored.] We call this the ID (independent diffusion) model. HF consider this problem both analytically and numerically. The proper boundary condition is trivially included in the finite difference method. The force free (FF) diffusion model, which just includes the excluded volume effect as a reflecting boundary at $r = d$ [i.e. $g(r) = 0$ for $r < d$ and $g(r) = 1$ for $r > d$, where $g(r)$ is the pcf], may also be solved analytically by a modification of the earlier treatments. This is given by HF, who show that there is a small correction for $J(0)$, but the frequency dependences of the $J(\omega)$ at higher frequencies are considerably different for the two cases.

We wish, in the present work, to extend the analytic results of HF for the FF model, in which the boundary value condition arising from the excluded volume is treated correctly, to the cases where (1) one spin is rapidly relaxing due to a short T_1^S and T_2^S (we let S rep-

resent the independently relaxing spin and I the spin that is being studied); (2) the diffusion is described by Torrey-like³ finite jumps; and (3) the diffusion coefficient is allowed to be frequency dependent. Case (1) was treated by Pfeiffer⁶ for the ID model, while case (2) is given by Torrey³ for the ID model. Case (3) is based on a recent theory of Hwang and Freed.⁷ We discuss the results for the FF model.

I. FINITE T_1^S and T_2^S

The correlation function $G(t)$ for the FF model is given by Eq. (A9) of I. The spectral density is defined as⁸

$$J_k(\omega) = 2 \operatorname{Re} \int_0^\infty G(t) e^{-i\omega t + (T_k^S)^{-1} t} dt, \quad k = 1, 2. \quad (1)$$

The results in I are given for $(T_k^S)^{-1} = \epsilon \rightarrow 0^+$. However, by letting $\epsilon \rightarrow T_k^S$ in the Fourier transformation we obtain the $J(\omega)$ needed for spin relaxation between the unlike spins S and I . One finds [cf. Eqs. (A11)–(A13) of I] that⁸

$$J_k(\omega) = \frac{8}{27} \frac{\eta_b}{dD} \times \operatorname{Re} \left[\frac{1 + \frac{1}{4} (i\omega\tau + \tau/T_k^S)^{1/2}}{1 + (i\omega\tau + \tau/T_k^S)^{1/2} + \frac{1}{9} (i\omega\tau + \tau/T_k^S) + \frac{1}{9} (i\omega\tau + \tau/T_k^S)^{3/2}} \right], \quad k = 1, 2, \quad (2)$$

where $\tau \equiv d^2/D$, and $D = D_a + D_b$, the sum of the diffusion coefficients of molecules a and b bearing spins I and S , respectively. Also, η_b is the number density of b molecules. As we have pointed out in I, the use of the correct boundary condition leads to much simpler expressions than the ID case (cf. the results of Hubbard⁵ in the absence of T_1 effects and the results of Pfeiffer⁶ including them, both of which involve transcendental functions). In the limit $|\omega T_k^S| \ll 1$ one has

$$J_k(\omega) \cong J(0) = \frac{8}{27} \frac{\eta_b}{dD} \times \left[\frac{1 + \frac{1}{4} (\tau/T_k^S)^{1/2}}{1 + (\tau/T_k^S)^{1/2} + \frac{1}{9} (\tau/T_k^S) + \frac{1}{9} (\tau/T_k^S)^{3/2}} \right] \xrightarrow{\tau/T_k^S \gg 1} \frac{2}{3} \frac{\eta_b}{d^3} T_k^S. \quad (3)$$

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Another convenient limit is $|\omega T_k^S| \gg 1$, which yields

$$J(\omega) = \frac{8}{27} \frac{\eta_b}{dD} \left[\frac{1 + (5/4\sqrt{2})(\omega\tau)^{1/2} + \frac{1}{4}(\omega\tau)}{1 + \sqrt{2}(\omega\tau)^{1/2} + (\omega\tau) + (2/3\sqrt{2})(\omega\tau)^{3/2} + (8/81\sqrt{2})(\omega\tau)^{5/2} + (\omega\tau)^3/81} \right]$$

$$\xrightarrow{\omega\tau \ll 1} \frac{8}{27} \frac{\eta_b}{dD} \left[1 - \frac{3}{8} \left(\frac{2\omega d^2}{D} \right)^{1/2} \right]$$

$$\xrightarrow{\omega\tau \gg 1} 6\eta_b D / (\omega d^2)^2$$
(4)

and are just the results of I [cf. Eq. (A13) of I]. These results are both simpler as well as sounder mathematically than those previously given.

II. JUMP DIFFUSION

One now may introduce isotropic molecular jumps for each molecular species (e.g., the b molecules) according to the exponential distribution

$$A_b(r) = (4\pi D_b \tau_{bj} r)^{-1} \exp[-r/(D_b \tau_{bj})^{1/2}],$$
(5a)

where $A_b(r)$ is the probability of a jump of magnitude r in a single step, while τ_{bj} is the mean time between jumps, and $D_b \tau_{bj} = \langle r_b^2 \rangle / 6$, where $\langle r_b^2 \rangle$ is the mean square jump distance. Its Fourier transform is

$$A_b(\rho) = 1/(1 + D_b \tau_{bj} \rho^2).$$
(5b)

This is the distribution used by Torrey,³ which reduces to Brownian diffusion in the limit $D_b \tau_{bj} \rightarrow 0$. The correct conditional probability distribution for the FF model involving relative diffusion of a and b molecules may now be written as^{1,3}

$$P(\mathbf{r}, |\mathbf{r}_0, t) = \frac{1}{\sqrt{r r_0} 4\pi} \int_0^\infty \exp[-Dt\rho^2/(1 + D\tau_j \rho^2)] \rho d\rho \sum_L (2L+1) P_L(\cos\theta) F_{L+(1/2)}(\rho r) F_{L+(1/2)}(\rho r_0),$$
(6)

where the $F_{L+(1/2)}(\rho r)$ are the correct modified Bessel Functions for a reflecting-wall boundary at $r=d$ and are given in I. Here we again have $D = D_a + D_b$, but we have set $\langle r_a^2 \rangle = \langle r_b^2 \rangle \equiv 6D\tau_j$ for the simple form of the exponential in Eq. (6). One then has the following for $G(t)$:

$$G(t) = \eta_b \int_0^\infty \rho d\rho \exp[-Dt\rho^2/(1 + D\tau_j \rho^2)] \times \int_d^\infty \frac{F_{5/2}(\rho r)^2}{r^{3/2}} = \frac{18\eta_b}{\pi d^3} \int_0^\infty \chi^2 d\chi \exp[-(\chi^2 t/\tau)/(1 + \chi^2 \tau_j/\tau)]$$

$$\times \left[\frac{A}{\chi^2 + a} + \frac{B}{\chi^2 + b} + \frac{B^*}{\chi^2 + b^*} \right]$$
(7)

by the methods of I. Here $a = 3.1800$, $b = -2.5900 + i4.3318$, and b^* is the complex conjugate of b .⁹ Also $2B = i[(a-b)\text{Im}b]^{-1}$ and $A = -B - B^* = -2\text{Re}B$, where again $\tau \equiv d^2/D$ and $\chi = \rho^2/d$. $G(t)$ is obtained explicitly in I for the limit $D\tau_j \rightarrow 0$. Here it is better to first take the Fourier transform of Eq. (1), and then to perform the integration over χ . This is straightforward, and one obtains

$$J_k(\omega) = J_k'(\omega) + J_k''(\omega)$$
(8)

where

$$J_k'(\omega) = \frac{8}{27} \frac{\eta_b}{dD} \text{Re} \left[\left(\frac{1}{1 + s_k \tau_j} \right) \frac{1 + (\bar{\sigma}_k/4)}{1 + \bar{\sigma}_k + (4\bar{\sigma}_k^2/9) + (\bar{\sigma}_k^3/9)} \right]$$
(9a)

and

$$J_k''(\omega) = \frac{8\eta_b}{27dD} \left(\frac{\tau_j}{\tau} \right) \text{Re} \left[\left(\frac{1}{1 + s_k \tau_j} \right) \frac{9/4 - (5\bar{\sigma}_k^2/4) + (3\bar{\sigma}_k^3/4) - \bar{\sigma}_k^4/4}{1 - \bar{\sigma}_k^2/9 - (2\bar{\sigma}_k^4/81) - (\bar{\sigma}_k^6/81)} \right],$$
(9b)

where the definitions $\bar{\sigma}_k^2 \equiv s_k \tau / (1 + s_k \tau_j)$ and $s_k \equiv i\omega + T_k^{S-1}$ with $k=1$ or 2 have been introduced. Note $\tau_j/\tau = \langle r^2 \rangle / 6d^2$, so in the Brownian limit $\tau_j/\tau \rightarrow 0$, $J''(\omega) \rightarrow 0$, and $J'(\omega)$ gives the result Eq. (4) [or Eq. (A13) of I] for $T_k^{S-1} = 0$, or of Eq. (2) for finite T_k^S , $k=1$ or 2 . Note also in the limit $s \rightarrow 0$ (i.e., zero frequencies and no T_1 or T_2 effects) one obtains

$$J(0) = \frac{8}{27} \frac{\eta_b}{dD} \left(1 + \frac{3}{8} \frac{\langle r^2 \rangle}{\langle d^2 \rangle} \right).$$
(10)

This result may be compared with the Torrey result for ID as given by HM,² but in the present notation

$$J(0)^{\text{ID}} = \frac{4}{15} \frac{\eta_b}{dD} \left(1 + \frac{5}{12} \frac{\langle r^2 \rangle}{\langle d^2 \rangle} \right).$$
(11)

Also, it is easy to obtain the frequency-dependent $J(\omega)$ which are affected by the finite jump correction. Thus, to lowest orders in ω , and neglecting T_k , one obtains¹¹

$$J(\omega) = \frac{8}{27} \frac{\eta_b}{Dd} \left[1 + \frac{3}{8} \frac{\langle r^2 \rangle}{d^2} - \frac{3}{8} \left(\frac{2\omega d^2}{D} \right)^{1/2} + \frac{1}{2} \left(\frac{1}{9} + \frac{3}{32} \frac{\langle r^2 \rangle}{d^2} \right) \left(\frac{2\omega d^2}{D} \right)^{3/2} \right] + O(\omega^2). \quad (12)$$

The case for $\omega=0$ and $s=(T_k^S)^{-1}$ is easily obtained from Eqs. (8) and (9), and in the limit $(T_k^S)^{-1} \rightarrow 0$ one has

$$J_k(0) = \frac{8}{27} \frac{\eta_b}{dD} \left[1 + \frac{3}{8} \frac{\langle r^2 \rangle}{d^2} - \frac{3}{4} \left(\frac{d^2}{T_k^S D} \right)^{1/2} - \frac{1}{3T_k^S D} \left(\langle r^2 \rangle + \frac{25}{12} d^2 + \frac{3}{16} \frac{\langle r^2 \rangle^2}{d^2} \right) \right] + O(T_k^S)^{-3/2}. \quad (13)$$

(The case where $\langle r_a^2 \rangle \neq \langle r_b^2 \rangle$ is more complex, but could be treated by properly generalizing the above analysis.) The fact that $J(0)$ is sensitive to the model of jump diffusion is probably due to the mixing in of many diffusional eigenvalues¹²: $D\rho^2/[1+D\tau_j\rho^2]$ of Eq. (6). This is in marked contrast to the rotational diffusion problem.¹³ We may also note that in the limit: $\omega \rightarrow \infty$, Eqs. (8) and (9) yield an asymptotic dependence of $J_k(\omega) \propto 1/\omega^2$ just as was obtained in Eq. (4); while for $T_k^S \rightarrow 0$, these equations yield $J_k(\omega) \propto T_k^S$ as in Eq. (3). However, the coefficients are considerably modified by the jump diffusion.

III. FREQUENCY-DEPENDENT DIFFUSION COEFFICIENT

Hwang and Freed have introduced a non-Brownian correction to the simple diffusion model.⁷ It corrects for the finite lifetime of the fluctuating forces generating the diffusion compared to $\tau = D^2/d$, and is appropriate in the limit of long-enough times (or short-enough frequencies) that inertial effects on the motion are unimportant. If the correlation function of the fluctuating forces is assumed to have a simple exponential decay with decay constant τ_M , then one has⁷

$$D(\omega) \approx D^0(1+i\omega\tau_M), \quad (14)$$

which yields a conditional probability similar to (but not identical to) Eq. (6). The two forms are compared by Hwang and Freed,¹⁴ and one easily shows that the result for this case is given by

$$J(\omega) = J'(\omega), \quad (15)$$

where $J'(\omega)$ is again given by Eq. (9a) but with $\tau_j \rightarrow \tau_M$, and $D \rightarrow D^0$, where D^0 is the conventional zero-frequency spectral density. Thus it yields the result of Eq. (3) for $\omega = T_k^{-1} = 0$, and in general will yield new corrections to $J(\omega) \neq J(0)$ in terms of powers of $\tau_M\omega$ and τ_M/T_k . (Note the Brownian motion limit is $\tau_M \rightarrow 0$.)

IV. SUMMARY

We found that a correct analysis of the excluded-volume effect allows for relatively simple expressions for the jump diffusion mechanism as well as for effects of finite T_k^S . Also, while Hwang and Freed noted the formal similarities between jump diffusion and a frequency-dependent diffusion coefficient, they do lead to different detailed predictions. However, it was shown in I that effects of equilibrium pcf's on the diffusive motion can indeed lead to significant corrections to $J(\omega)$ and $J(0)$: hard sphere or attractive intermolecular potentials will lead to an increase in $J(0)$ [while repulsive

potentials will decrease $J(0)$]. Also, dynamic flow processes, which can lead to an apparent position-dependent diffusion coefficient such that the relative motion slows as molecules approach [and which has been treated for CIDE(N)P¹⁵], would be expected to enhance $J(0)$. We note that only for frequencies ω such that $J(\omega) \neq J(0)$ can model effects from a frequency-dependent diffusion coefficient be observed; (alternatively, one can replace a finite ω by a finite $(T_k^S)^{-1}$, $k=1, 2$ to achieve this same qualitative conclusion).

The combined effects of finite pcf, dynamic diffusive processes, jump diffusion, and finite $(T_k^S)^{-1}$ can be treated by finite difference methods as given in I and at considerable length in the review by Pedersen and Freed.¹⁶

¹L. P. Hwang and J. H. Freed, *J. Chem. Phys.* **63**, 4017 (1975); referred to as I.

²J. F. Harmon and B. H. Muller, *Phys. Rev.* **182**, 400 (1969).

³H. C. Torrey, *Phys. Rev.* **92**, 962 (1953).

⁴A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University, Oxford, 1961), Chap. VIII.

⁵P. S. Hubbard, *Proc. R. Soc. (London) Ser. A* **291**, 537 (1966).

⁶H. Pfeifer, *Ann. Phys. (Leipzig)* **8**, 1 (1961).

⁷L. P. Hwang and J. H. Freed, *J. Chem. Phys.* **63**, 118 (1975).

⁸Note that our $J(\omega)$ corresponds to Abragam's $J(\omega)$ of Eqs. (114) (Ref. 4, p. 302) except, as defined, his D is half our $D = D_a + D_b$. The typical equations for $(T_k^I)^{-1}$ due to dipolar relaxation by unlike spins are given by Eqs. (88) of Ref. 4. In our present notation

$$J^0(0)^A \rightarrow \frac{48\pi}{15} J_1(0); \quad J^0(\omega_I - \omega_S)^A \rightarrow \frac{48\pi}{15} J_2(\omega_I - \omega_S);$$

$$J^{(1)}(\omega_I)^A \rightarrow \frac{8\pi}{15} J_1(\omega_I); \quad J^{(1)}(\omega_S)^A \rightarrow \frac{8\pi}{15} J_2(\omega_S);$$

$$J^{(2)}(\omega_I + \omega_S)^A \rightarrow \frac{32\pi}{15} J_2(\omega_I + \omega_S),$$

where the superscript A indicates Abragam's notation [cf. L. P. Hwang, C. V. Krishnan, and H. L. Friedman, *Chem. Phys. Lett.* **20**, 391 (1973)].

⁹In I a sign for b is misprinted. Note also from I that $a|b|^2 = 81$, $a+b+b^* = -2$, and $2a\text{Re}b + |b|^2 = 9$.

¹⁰J. G. Hexem, U. Edlund, and G. C. Levy, *J. Chem. Phys.* **64**, 936 (1976).

¹¹Note a factor of $\sqrt{2}$ missing in Eq. (A15) of I.

¹²P. A. Egglestaff, *An Introduction to the Liquid State* (Academic, New York, 1967).

¹³It is well known that in the somewhat analogous problem of rotational diffusion by finite jumps [E. N. Ivanov, *Sov. Phys. JETP* **18**, 1041 (1964)] a spin relaxation observable in the

motional narrowing region will just yield the rotational diffusion coefficient D_R , the definition of which is in terms of the rms jump angle.

¹⁴Reference 7, Eqs. (5.17) and (5.18).

¹⁵J. B. Pedersen and J. H. Freed, *J. Chem. Phys.* **62**, 1790

(1975).

¹⁶J. H. Freed and J. B. Pedersen, *Adv. Magn. Reson.* **8**, 1 (1976). This review includes explicit finite difference expressions for the jump diffusion model, including the reflecting-wall boundary at $r=d$.