

# Dynamic effects of pair correlation functions on spin relaxation by translational diffusion in liquids\*

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(Received 17 June 1975)

It is shown how the equilibrium pair correlation function between spin-bearing molecules in liquids may be incorporated as an effective force in the relative diffusion expressions, and how one may solve for the resulting time correlation functions and spectral densities needed for studies of spin relaxation by translational diffusion. The use of finite difference methods permits the solution no matter how complex the form of the pair correlation function (pcf) utilized. In particular, a Percus-Yevick pcf as well as one corrected from computer dynamics, both for hard spheres, are utilized. Good agreement with the experiments of Harmon and Muller on dipolar relaxation in liquid ethane is obtained from this analysis. Effects of ionic interactions in electrolyte solutions upon dipolar relaxation are also obtained in terms of Debye-Hückel theory for the pcf. Analytic solutions are given which are appropriate for the proper boundary-value problem for the relative diffusion of molecules (i.e., a distance of minimum approach) that has usually been neglected in the spin relaxation theories. Other molecular dynamics aspects of spin relaxation by translational diffusion in liquids are briefly discussed.

## I. INTRODUCTION

It is appreciated by many workers that studies of spin relaxation by translational diffusion will reflect the molecular details of liquid state structure and dynamics.<sup>1-4</sup> In an early and pioneering theoretical work, Torrey<sup>1</sup> showed how such studies could reflect the extent to which the molecular diffusion occurs by random flights or "jump diffusion" instead of the limiting model of continuous Brownian diffusion. Harmon and Muller applied these ideas of Torrey to careful experiments on liquid ethane.<sup>2</sup> In their work, they removed the assumption that the diffusive process is uniform by recognizing that the equilibrium distribution of spin-bearing molecules should be represented by well-chosen pair-correlation functions or radial distribution functions. While they used a simple hard-sphere radial distribution function in the low density limit, other workers have considered more complex pair-correlation functions, e.g., models appropriate for charged ions in electrolyte solutions.<sup>3,4</sup>

However, for the most part in the previous work on liquids, the pair-correlation function was only used to describe the initial equilibrium distribution. The time-dependent behavior of the interacting spin-dependent molecules was still treated in terms of conditional probability functions or Green's functions which characteristically yield uniform distributions in the long-time limit, i.e., they ignore pair-correlation effects. The inclusion of pair-correlation effects into the dynamical time evolution of the translational diffusion is not a simple matter, but one which is clearly necessary in order to more appropriately analyze and interpret the experiments. Once one interprets the pair-correlation function as related to a potential of averaged forces between the spin-bearing molecules, one may then obtain the associated effective force between them. It then becomes necessary to describe their relative diffusion by an appropriate (generalized) diffusion equation which also includes the effective forces. It is the solution of such expressions which poses very considerable analytical difficulties, not to mention the final calculation of the relevant spin correlation functions and spectral densities.

It is a major objective of the present work to demonstrate how recently developed finite-difference techniques<sup>5</sup> can readily and successfully be employed to give explicit solutions for the spin-correlation functions and spectral densities from typical diffusion equations even when the pair-correlation functions, hence the resulting effective forces, are so complex as to be only known in numerical form. In this work we emphasize, in particular, spin relaxation by intermolecular spin-dipolar interactions. Furthermore, we pay special attention to the selection of good pair-correlation functions for liquid ethane in order to compare our results with the experiments of Harmon and Muller. The soundest pair-correlation functions we employ here are based on hard-sphere solutions to the Percus-Yevick equation<sup>6</sup> as well as the appropriate corrections indicated by the computer-dynamics studies of Verlet and Weis.<sup>7</sup> These pair-correlation functions, which adequately represent the denseness of liquid ethane, indicate clearly that the low-density limiting form used by Harmon and Muller is not at all adequate.

We also illustrate our approach with examples for ionic solutions using Debye-Hückel theory for the pair-correlation functions.

As we have already noted, the Green's functions typically employed previously are consistent with a uniform equilibrium distribution. They even neglect the boundary value problem due to a distance of closest approach (the "independent diffusion" model). It is possible, however, to obtain analytically the Green's functions which properly include this boundary in the case of simple Brownian diffusion under an otherwise uniform pair-correlation function (i.e., a "force-free" diffusion). The appropriate expressions, including the spin-correlation functions and spectral densities, are given in Appendix A both for dipolar relaxation and for a model of relaxation by a scalar interaction of finite range proposed by Hubbard.<sup>8</sup> The analytical result for dipolar relaxation is employed to check the accuracy and convergence of our finite difference method for this simple model.

## II. SPECTRAL DENSITY AND CORRELATION FUNCTION FOR DIPOLAR RELAXATION

The space-dependent time-correlation function for dipolar interaction between spins 1 and 2 may be expressed by<sup>9</sup>

$$G(t) = \frac{5}{4\pi} \mathfrak{N} \int d^3r \int d^3r_0 \mathfrak{D}_{0m}^{(2)*}(\Omega_r) \mathfrak{D}_{0m}^{(2)}(\Omega_{r_0}) \times P(\mathbf{r}_0 | \mathbf{r}, t) g(r_0) / r_0^3 r^3, \quad (2.1)$$

where  $G(t)$  is a real and even function of  $t$ , and its spectral density is given by

$$J(\omega) = 2 \operatorname{Re} \int_0^\infty e^{i\omega t} G(t) dt. \quad (2.2)$$

In Eqs. (2.1) and (2.2),  $\mathfrak{N}$  is the average number density of spins and  $P(\mathbf{r}_0 | \mathbf{r}, t)$  is the conditional probability for the relative diffusion of spins 1 and 2; i. e., given these spins are separated by  $\mathbf{r}_0$  at  $t=0$ , it gives the probability they are separated by  $\mathbf{r}$  at time  $t$ . Also,  $\Omega_r$  is the solid angle between the intermolecular vector  $\mathbf{r}$  and the laboratory coordinate frame, etc. We now approximate  $P(\mathbf{r}_0 | \mathbf{r}, t)$  as the solution of the Smoluchowski equation,<sup>10,11</sup> i. e.,

$$\frac{\partial P(\mathbf{r}_0 | \mathbf{r}, t)}{\partial t} = D \nabla \cdot \left[ \nabla P(\mathbf{r}_0 | \mathbf{r}, t) + \frac{1}{kT} P(\mathbf{r}_0 | \mathbf{r}, t) \nabla U(r) \right], \quad (2.3)$$

with initial condition

$$\lim_{t \rightarrow 0} P(\mathbf{r}_0 | \mathbf{r}, t) = \delta(r - r_0). \quad (2.4)$$

In Eq. (2.3),  $D$  is the diffusion coefficient for relative diffusion,

$$D \equiv D_1 + D_2, \quad (2.5)$$

and  $U(r)$  is the potential of averaged forces between the spin-bearing molecules 1 and 2. We assume for simplicity that it only depends upon the radial separation and is independent of the molecular orientations. A more general discussion of the applicability of the Smoluchowski equation for relative diffusion of molecules and possible improvements on it is given elsewhere.<sup>11</sup> We are also neglecting any hydrodynamic effects in Eq. (2.3) which would lead to an apparent space-dependent diffusion equation.<sup>12</sup> Then we may obtain  $U(r)$  from the pair-correlation function  $g(r)$ , i. e.,

$$\ln g(r) \equiv -U(r)/kT, \quad (2.6a)$$

so that one has an effective force

$$\mathbf{F}(r) \equiv -(\nabla U(r))/kT = \nabla(\ln g(r)). \quad (2.6b)$$

The expressions of Eqs. (2.6) when incorporated into Eq. (2.3) then means that in the limit  $t \rightarrow \infty$ ,  $P(\mathbf{r}_0 | \mathbf{r}, t)$  will yield the equilibrium  $g(r)$ , while, for finite times,  $\mathbf{F}(r)$  is the driving force acting to restore this equilibrium. It is convenient for purposes of solution to break up the  $g(r)$  into two parts: (1) the hard core, zero-concentration part, which we approximate in this work by a hard sphere model, and (2) the more long range interactions and concentration-dependent contributions. The effect of the former may be replaced by a reflecting wall

boundary condition as discussed in Appendix B, while the latter is explicitly included in the  $F(r)$  appropriate for the different models (cf. Sec. III).

Now the rhs of Eq. (2.3) may be separated into orientational and radial parts. It gives

$$[\nabla \cdot (\nabla - \mathbf{F}(r))] P(\mathbf{r}_0 | \mathbf{r}, t) = \left( \Gamma_r + \frac{1}{r^2} \Gamma_\Omega \right) P(\mathbf{r}_0 | \mathbf{r}, t), \quad (2.7)$$

where

$$\Gamma_r P(\mathbf{r}_0 | \mathbf{r}, t) = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \frac{\partial}{\partial r} P(\mathbf{r}_0 | \mathbf{r}, t) \right] - \frac{1}{r^2} \frac{\partial}{\partial r} [r^2 F(r) P(\mathbf{r}_0 | \mathbf{r}, t)] \quad (2.8a)$$

with  $F(r) = |\mathbf{F}(r)|$  and

$$\Gamma_\Omega P(\mathbf{r}_0 | \mathbf{r}, t) = + \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left[ \sin \theta \frac{\partial}{\partial \theta} P(\mathbf{r}_0 | \mathbf{r}, t) \right] + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} P(\mathbf{r}_0 | \mathbf{r}, t) \right\}. \quad (2.8b)$$

The Fourier-Laplace transform of Eq. (2.3) gives

$$- \left[ D \left( \Gamma_r + \frac{1}{r^2} \Gamma_\Omega \right) + i\omega \right] \tilde{P}(\mathbf{r}_0 | \mathbf{r}, \omega) = \delta(r - r_0), \quad (2.9)$$

where

$$\tilde{P}(\mathbf{r}_0 | \mathbf{r}, \omega) \equiv \int_0^\infty e^{i\omega t} P(\mathbf{r}_0 | \mathbf{r}, t) dt. \quad (2.10)$$

When we multiply Eq. (2.9) with  $\mathfrak{D}_{0m}^{(2)}(\Omega_0) g(r_0) / r_0^3$  and then integrate it over  $\mathbf{r}_0$  space, we obtain

$$\int \frac{\mathfrak{D}_{0m}^{(2)}(\Omega_{r_0}) g(r_0)}{r_0^3} \tilde{P}(\mathbf{r}_0 | \mathbf{r}, \omega) d^3r_0 = \mathfrak{D}_{0m}^{(2)}(\Omega_r) \left[ D \left( -\Gamma_r + \frac{6}{r^2} \right) - i\omega \right]^{-1} g(r) / r^3 \quad (2.11)$$

since  $\Gamma_\Omega \mathfrak{D}_{0m}^{(2)}(\Omega_r) = -l(l+1) \mathfrak{D}_{0m}^{(2)}(\Omega_r)$ . Then we multiply Eq. (2.11) with  $\mathfrak{D}_{0m}^{*(2)}(\Omega_r) / r^3$  and integrate over  $\mathbf{r}$  space, and we obtain, in accordance with Eqs. (2.1) and (2.2),

$$J(\omega) = 2\mathfrak{N} \operatorname{Re} \int dr \frac{1}{r} \left[ D \left( -\Gamma_r + \frac{6}{r^2} \right) - i\omega \right]^{-1} \frac{g(r)}{r^3} \equiv 2\mathfrak{N} \operatorname{Re} \int dr \frac{1}{r} q(r, \omega) \equiv 2\mathfrak{N} \operatorname{Re} \int dr \frac{1}{r^2} \hat{q}(r, \omega), \quad (2.12)$$

where we define

$$\hat{q}(r, \omega) \equiv r q(r, \omega) \equiv \left[ D \left( -\hat{\Gamma}_r + \frac{6}{r^2} \right) - i\omega \right]^{-1} \frac{g(r)}{r^2} \quad (2.13)$$

with the modified operator  $\hat{\Gamma}_r$ ,

$$\hat{\Gamma}_r \hat{q}(r, \omega) \equiv \frac{\partial^2}{\partial r^2} \hat{q}(r, \omega) - \frac{1}{r} \frac{\partial}{\partial r} [r F(r) \hat{q}(r, \omega)]. \quad (2.14)$$

The spectral density based on Eq. (2.12) is to be evaluated by finite difference methods, e. g.,

$$\frac{\partial}{\partial r} \hat{q}(r, \omega) \rightarrow \frac{\hat{q}(r + \Delta r, \omega) - \hat{q}(r - \Delta r, \omega)}{2\Delta r} \quad (2.15a)$$

and

$$\frac{\partial^2 \hat{q}(r, \omega)}{\partial r^2} - \frac{\hat{q}(r + \Delta r, \omega) - 2\hat{q}(r, \omega) + \hat{q}(r - \Delta r, \omega)}{(\Delta r)^2}. \quad (2.15b)$$

Equation (2.13) may then be rewritten in a matrix form as

$$[(-\mathbf{W} + \mathbf{B}) - i\omega \mathbf{1}] \mathbf{Q} = \mathbf{R}, \quad (2.16)$$

where  $\mathbf{Q}$  and  $\mathbf{R}$  are column vectors given by

$$\mathbf{Q} = \begin{bmatrix} \hat{q}(r_1, \omega) \\ \hat{q}(r_2, \omega) \\ \vdots \\ \hat{q}(r_m, \omega) \\ \vdots \\ \hat{q}(r_n, \omega) \end{bmatrix}, \quad \mathbf{R} = \begin{bmatrix} g(r_1)/r_1^2 \\ g(r_2)/r_2^2 \\ \vdots \\ g(r_m)/r_m^2 \\ \vdots \\ g(r_n)/r_n^2 \end{bmatrix}. \quad (2.17)$$

The  $\mathbf{W}$  matrix is a "transition-probability" matrix between discrete values of  $r$  and has been discussed in detail by Pedersen and Freed.<sup>5</sup> The matrix elements are given by the following set of equations:

$$D^{-1}W_{0,0} = -2/(\Delta r)^2 (1 + \Delta r/d) - r_1 F(1)/(d\Delta r), \quad (2.18a)$$

$$D^{-1}W_{0,1} = 2/(\Delta r)^2 - F(0)/\Delta r, \quad (2.18b)$$

$$D^{-1}W_{j,j-1} = \Delta r^{-2} + F(j)/(2\Delta r), \quad (2.18c)$$

$$D^{-1}W_{j,j} = -2/\Delta r^2 - [F(j+1)r_{j+1} - F(j-1)r_{j-1}]/(2r_j \Delta r), \quad (2.18d)$$

$$D^{-1}W_{j,j+1} = \Delta r^{-2} - F(j)/(2\Delta r), \quad (2.18e)$$

where  $0 < j < M$ , and

$$D^{-1}W_{M,M-1} = 2/(1+f)\Delta r^2 + F(M)/(1+f)\Delta r, \quad (2.19a)$$

$$D^{-1}W_{M,M} = -2/f\Delta r^2 + F(M-1)r_{M-1}/r_M(1+f)\Delta r, \quad (2.19b)$$

$$D^{-1}W_{M,M+1} = 2/f(1+f)\Delta r^2, \quad (2.19c)$$

while for  $M < j < N$ ,

$$D^{-1}W_{j,j-1} = 1/(f\Delta r)^2, \quad (2.20a)$$

$$D^{-1}W_{j,j} = -2/(f\Delta r)^2, \quad (2.20b)$$

$$D^{-1}W_{j,j+1} = 1/(f\Delta r)^2, \quad (2.20c)$$

and also

$$D^{-1}W_{N-1,N} = 0, \quad (2.21a)$$

$$D^{-1}W_{N,N-1} = 2/(f\Delta r)^2, \quad (2.21b)$$

$$D^{-1}W_{N,N} = 0. \quad (2.21c)$$

In Eq. (2.16) the matrix  $\mathbf{B}$  is a diagonal matrix with elements  $B_{i,i} = 6D/r_i^2$ . In Eqs. (2.18)–(2.21),  $r_0 = d$  is the "distance of closest approach" between particles 1 and 2, which usually is chosen as the sum of the crystal radii or another appropriate distance parameter;  $\Delta r$  is the distance between the  $j$ th and  $(j-1)$ th adjacent positions, where  $j < M$ . Also,  $M$  is chosen such that for  $r > r_M$ , we have  $g(r) \sim 1$  and  $F(r) \sim 0$ , and the contribution to the relaxation for  $r > r_M$  is small and smoothly varying in space. Therefore, for  $j > M$ , we choose the difference  $r_{j+1} - r_j = f\Delta r$ , where  $f$  is about 10 to 25, to conveniently extend the range of calculation and yet not lose accuracy. In addition we have  $r_1 - r_0 = \Delta r/2$ ,  $r_{M+1} - r_M = (1+f)\Delta r/2$ ,

and  $r_N - r_{N-1} = f\Delta r/2$ . The choices of those differences and the elements in the zeroth,  $M$ th, and  $N$ th rows of  $\mathbf{W}$  are required in order to satisfy the conservation of total probability given by

$$\frac{\partial}{\partial t} \int d^3r P(\mathbf{r}, t) = 0. \quad (2.22a)$$

Thus, by Eq. (2.3) we have

$$\begin{aligned} 0 &= \int d^3r D \nabla \cdot [\nabla P - F(r)P] \\ &= 4\pi D \int dr r^2 \Gamma_r P \\ &= 4\pi D \int dr r \hat{\Gamma}_r(rP) \\ &= 4\pi D \sum_{ij} \Delta r_i r_i W_{i,j}(rP)_j. \end{aligned} \quad (2.22b)$$

Since  $(rP)_j$  is arbitrary, we obtain

$$\sum_i \Delta r_i r_i W_{i,j} = 0 \text{ for } j = 0, 1, \dots, M, \dots, N. \quad (2.23)$$

The above-noted matrix elements of  $\mathbf{W}$  have been chosen to satisfy Eq. (2.23) exactly. This condition for  $j=0$  is equivalent to a reflecting-wall boundary condition at  $d$  for  $F(r) = 0$ ; i. e.,  $\partial P/\partial r|_{r=d} = 0$  cf Appendix B. The zero matrix elements for  $j=N$  yield an outer absorbing (or collecting) wall. This outer boundary condition was most successful in yielding convergent results for not too large values of  $r_N$ .

The spectral density  $J(\omega)$  may be written in finite difference notation as

$$J(\omega) = 2\Re \sum_{i=0}^N \frac{\Delta r_i}{r_i^2} (\text{Re}Q_i), \quad (2.24)$$

where  $\text{Re}Q_i$  is the solution of the matrix equation

$$\{[-\mathbf{W} + \mathbf{B}]^2 + \omega^2 \mathbf{1}\} (\text{Re}Q) = [-\mathbf{W} + \mathbf{B}] \mathbf{R}. \quad (2.25)$$

Alternatively, Eq. (2.16) may be solved by diagonalization methods, i. e., one may diagonalize the matrix sum  $-\mathbf{W} + \mathbf{B} \equiv \mathbf{C}$ . It is convenient first to convert this matrix to symmetric form represented by  $\tilde{\mathbf{C}}$ . This may be done by standard methods provided  $W_{i-1,i}/W_{i,i-1} > 0$ . In order to achieve this, we let  $W_{N-1,N}/W_{N,N-1} < 10^{-10}$  instead of zero, and this has no effect on the final result.

Thus we let  $\mathbf{T}$  be the similarity transformation which diagonalizes  $\mathbf{C}$ , i. e.,

$$\mathbf{TCT}^{-1} = \mathbf{OSC}S^{-1}\mathbf{O}^{-1} = \mathbf{O}\tilde{\mathbf{C}}\mathbf{O} = \mathbf{c}, \quad (2.26)$$

where we have let  $\mathbf{T} = \mathbf{OS}$ , where  $\mathbf{S}$  is the real symmetrizing matrix and  $\mathbf{O}$  is a real orthogonal matrix. Equations (2.25) and (2.16) then become

$$J(\omega) = 2\Re \sum_{i,j,k=0}^N \frac{\Delta r_i}{r_i^2} (T^{-1})_{i,j} \frac{C_{jj}}{C_{jj} + \omega^2} T_{j,k} R_k. \quad (2.27)$$

The diagonalization scheme also lends itself to the computation of  $G(t)$ . One obtains

$$G(t) = \Re \sum_{i,j,k=0}^N \frac{\Delta r_i}{r_i^2} (T^{-1})_{i,j} \exp(-c_{jj}t) T_{j,k} R_k. \quad (2.28)$$

The accuracy and validity of these approaches will be discussed in the next section.

### III. PAIR CORRELATION FUNCTIONS

#### A. Hard-sphere model

First, we consider the simplest pair-correlation function (pcf), which only includes the excluded volume of the two molecules, i. e.,

$$g(r) = \begin{cases} 0 & \text{for } r < d \\ 1 & \text{for } r > d. \end{cases} \quad (3.1)$$

We refer to this as the force-free pcf. The analytic solution of this model for  $G(t)$  and  $J(\omega)$  is given by Eqs. (A9) and (A13) of Appendix A. In Table I, we show the agreement between the finite difference method and the analytic result with various data sets for  $J(0)$ . The calculation of  $J(\omega)$  by the finite difference method, as we have employed it, yields less than 1.5% error throughout the entire dispersion region shown in Fig. 1.

The dispersion curve for the spectral density,  $J(\omega)$  for the independent diffusion model, which neglects the boundary condition at  $r=d$ , is also shown in Fig. 1. It is smaller in magnitude than for the force-free model for small  $\omega$  but shows markedly different behavior at high  $\omega$ . The larger value of  $J(0)$  for the force-free model is probably due in part to the reflecting-wall condition  $dP/dr|_{r=d} = 0$ , which would increase the time the interacting molecules remain in contact at  $r=d$  and the dipolar interaction is a maximum (i. e., it increases the mean-square value of the interaction). (Recall that in the independent diffusion model, while there are trajectories for which  $r < d$ , that part of their contributions for which  $r < d$  is omitted in the calculations of the spectral density.) The markedly different behavior for the two models at large  $\omega$  may be explained by first recognizing this reflects behavior at short times. Then, according to the diffusion equation Green's function of Eq. (A1), at short times, the large  $\rho$  modes (with  $\rho$  the Fourier transform of  $\mathbf{r}$ ) dominate in importance. Then Eq. (A2) shows that as  $\rho d$  becomes large, one gets greater deviation between the two models (while for  $\rho d \rightarrow 0$ , they become identical).

The results for  $J(\omega)$  for the hard-sphere model pcf are also given in Fig. 1. In this model we use the exact solutions of the Percus-Yevick (PY) equation for this case by Wertheim and Thiele (WT).<sup>6</sup> The WT pcf is first evaluated in the range  $d$  to  $6d$  by the method suggested

TABLE I. Accuracy of finite difference approach compared to analytic result for force-free model.

$\Delta r/d \times 10^2$	$r_M/d$	$r_N/d$	$\frac{J(0)dD}{2\eta}$	Percent error
1.25	7.263	100.83	0.14777	-0.26
1.25	7.263	163.20	0.14860	+0.31
1.25	13.51	82.13	0.14717	-0.66
1.75	9.767	140.76	0.14857	+0.29
2.50	7.263	100.83	0.14904	+0.60
2.50	13.510	200.65	0.14947	+0.89
Analytic			0.14815 = $\frac{4}{27}$	

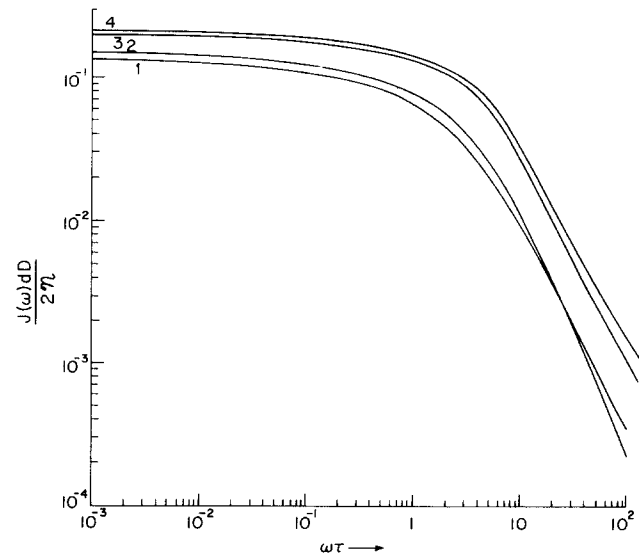


FIG. 1.  $\frac{1}{2}J(\omega)dD/\eta$  vs  $\omega\tau$  (where  $\tau \equiv d^2/D$ ) for dipolar relaxation for several different models: (1) "independent diffusion"; (2) force-free diffusion with boundary condition at  $d$ ; (3) hard-sphere Percus-Yevick, pcf with  $\eta = 0.578$  corresponding to  $d = 4.38 \text{ \AA}$  and  $\eta' = 0.656 \text{ gm/cm}^3$ ; (4) Verlet's modified hard-sphere Percus-Yevick, pcf with same parameters as (3).

by Throop and Bearman.<sup>13</sup> They use

$$g(r) = \frac{d}{12\eta r} \sum_{m=1}^{\infty} \frac{\theta(r-md)(-)^{m+1}}{(m-1)!} \sum_{i=1}^3 \lim_{y \rightarrow y_i} \frac{d^{m-1}}{dy^{m-1}} \times \left\{ (y-y_i)^m y \left[ \frac{L(y)}{S(y)} \right]^m \exp(y(r/d-m)) \right\} \quad (3.2)$$

for  $\pi\eta'd^3/6 \equiv \eta < 1$ , where  $\eta'$  is the average number density of molecules, and where

$$\theta(x) = \begin{cases} 1 & \text{for } x > 0 \\ 0 & \text{for } x < 0, \end{cases} \quad (3.3)$$

where  $S(y) = (1-\eta)^2 y^3 + 6\eta(1-\eta)y^2 + 18\eta^2 y - 12\eta(1+2\eta)$ ,  $L(y) = 12\eta[(1+\frac{1}{2}\eta)y + (1+2\eta)]$ , and  $y_i$  ( $i=1, 2, 3$ ) are the three roots of  $S(y)$ . For  $d < r < 3d$ , the results of Eq. (3.2) are readily differentiated to yield  $F(r)$ . However, for  $r > 3d$ , the analytic behavior of Eq. (3.2) becomes more unwieldy, so we computed  $F(r)$  for  $d < r < 6d$  by a finite difference method utilizing up through fourth order in the finite differences. The finite difference values for  $F(r)$  for  $d < r < 3d$  were in excellent agreement with the analytic result. Beyond  $6d$ , we let  $g(r) = 1$  and  $F(r) = 0$ . The results in Fig. 1 are for  $\eta = 0.578$ , which is the appropriate value for liquid ethane if we use  $d = 4.38 \text{ \AA}$  as did HM (but see below).

The main difference between the hard-sphere and force-free pair-correlation functions is in the large maximum for the former near the core at  $r=d$ . This has the effect of significantly enhancing the magnitude predicted for  $J(\omega)$ . This enhancement becomes more pronounced at higher  $\omega$ , again since the large  $\rho$  modes are more important and they reflect the shorter range interactions.

Verlet and Weis<sup>7</sup> have compared the PY theory with

detailed results from "exact" computer dynamics results. They have found a number of weaknesses with the WT pcf. In particular, (1) the pcf is too small near the core; (2) its oscillations for larger  $r$  have the consequence that the main maximum of the structure factor, equal to  $(1 + \pi' \int e^{ik \cdot r} [g(r) - 1] d^3r)$ , is too high; (3) the WT pcf oscillates slightly out of phase with respect to the pcf from computer experiments. Verlet and Weis have given a prescription for correcting the WT pcf to bring it into good agreement with the computer results. The results for  $J(\omega)$  for this modified WT pcf are also shown in Fig. 1. Since this modified  $g(r)$  is larger near the core than the WT  $g(r)$ , we see some increase in the resulting  $J(\omega)$ , and the effect becomes more pronounced at the higher frequencies.

## B. Electrolyte solutions

To explore the effect of ionic interactions on dipolar relaxation in liquids, we employed Debye-Hückel theory [sometimes also referred to as Debye-Hückel-Guntelberg (DHG)]<sup>4</sup>. It applies to the pcf in the sense that

$$U(r) = \frac{Z_1 Z_2}{\epsilon r} \frac{e^{-\kappa(r-d)}}{1 + \kappa d}, \quad (3.4)$$

where  $Z_1$  and  $Z_2$  are the charges on the spin-bearing ions 1 and 2, respectively, and where  $\kappa$ , the reciprocal thickness of the ionic layer, is given by

$$\kappa^2 = (8\pi e^2 I / \epsilon kT), \quad (3.5)$$

$$I = \frac{1}{2} \sum_i n_i Z_i^2,$$

where  $\epsilon$  is the dielectric constant of the medium,  $n_i$  is the number density of the  $i$ th type particle of charge  $Z_i$ , and  $I$  is the ionic strength. In Fig. 2, we calculate the spectral density for DHG models. The differences in

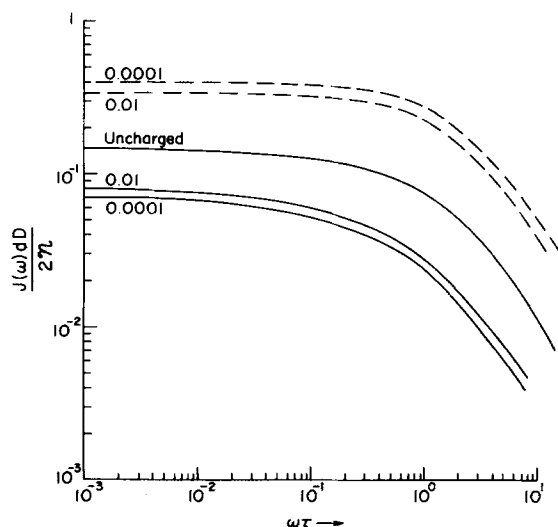


FIG. 2.  $\frac{1}{2} J(\omega) dD / \pi$  vs  $\omega \tau$  (where  $\tau \equiv d^2/D$ ) for dipolar relaxation of 1-1 electrolytes in aqueous solution at 25°C obeying Debye-Hückel theory. The ionic strengths in molarity units are listed on the figure. Also  $d = 4 \text{ \AA}$ . The solid lines are for repulsive forces, the dashed lines for attractive forces. The results for the uncharged force-free model are also shown.

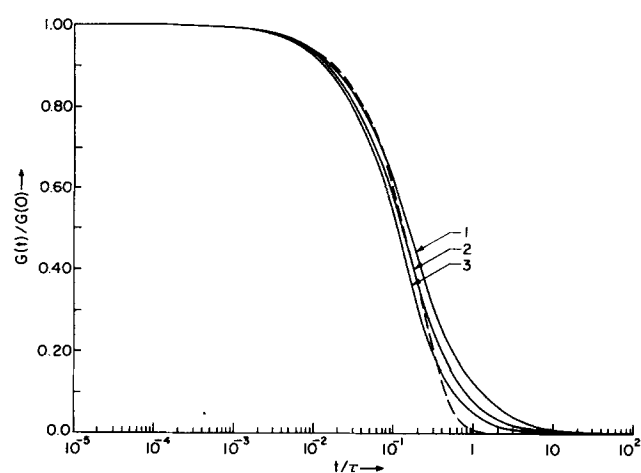


FIG. 3.  $G(t)/G(0)$  vs  $t/\tau$  (where  $\tau \equiv d^2/D$ ) for dipolar relaxation of 1-1 electrolytes in aqueous solution at 25°C obeying Debye-Hückel theory. Curves 1 (repulsive forces) and 3 (attractive forces) are for  $I = 0.0001 \text{ M}$ . Also  $d = 4 \text{ \AA}$ . Curve 2 is for the uncharged force-free model. The dashed curve is for  $e^{-5t/\tau}$ .

$J(\omega)$  show the effects of ionic strength and types of ionic charge.

Attractive (repulsive) forces are seen to lead to an enhancement (reduction) of  $J(\omega)$  over the force-free result, and the effect becomes more pronounced for larger  $\omega$ . We show in Fig. 3 computed  $G(t)$  results for these models. It is found that attractive (repulsive) forces result in more (less) rapid decay than the force-free result. We also show in Fig. 3 an exponentially decaying  $G(t)$  with correlation time  $0.2 \tau = 0.2 d^2/D$  for comparison purposes. It is seen that while this form agrees well with the correct results at short times, it cannot satisfactorily represent the  $G(t)$  for dipolar relaxation by translational diffusion. In particular, for long times it decays too fast compared to the typical  $t^{-3/2}$  dependence one obtains from the force-free diffusion models.

## IV. COMPARISON WITH EXPERIMENT

### A. $^1\text{H}$ relaxation in liquid ethane by translational diffusion

We show in Fig. 4 the experimental results for the low frequency dependence of  $T_1$  for liquid ethane obtained by Harmon and Muller (HM).<sup>2</sup> The  $T_1$  is related to the  $J(\omega)$  calculated for the different models in Sec. III according to the expression<sup>9</sup>

$$1/T_1 = \frac{4\pi}{5} \gamma_H^4 \hbar^2 I(I+1) [J(\omega) + 4J(2\omega)], \quad (4.1)$$

where  $\gamma_H$  is the gyromagnetic ratio of the proton and  $I = \frac{1}{2}$  is the proton spin quantum number. HM fit their experimental results (as shown in Fig. 4) with a  $d = 4.38 \text{ \AA}$  and a mean-square jump distance  $\langle r^2 \rangle$  given by  $\langle r^2 \rangle / d = 0.67$  and the independent diffusion model for the Green's function. Also, as we have noted in the Introduction, they used a  $g(r)$  appropriate in the low density limit. In particular, their  $g(r)$  has the value at the core of  $g(d) = 3.4$ , while the correct WT  $g(r)$  gives  $g(d) = 7.238$  (both

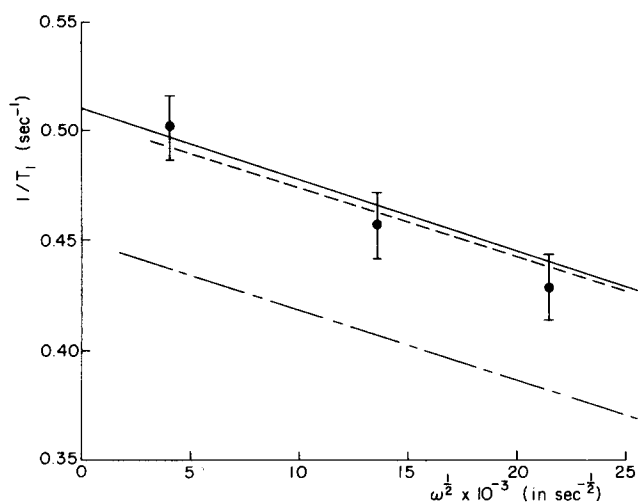


FIG. 4. Comparison of Harmon and Muller's experimental results on  $1/T_1$  vs  $\omega^{1/2}$  for liquid ethane with the theoretical predictions. The experimental points are shown with error bars. The solid line is the result of Harmon and Muller's calculation based upon an independent jump diffusion model and  $d=4.38$  Å. The dashed line is obtained in this work for the hard-sphere WT pcf with  $d=3.1$  Å,  $\rho=0.656$  gm/cm<sup>3</sup>, and  $\eta=0.2051$ , while the broken line is for the force-free model and  $d=3.1$  Å. Further details are given in the text.

for  $d=4.38$  Å), a large discrepancy considering the importance of the core value on  $J(\omega)$  [i. e., a larger  $g(d)$  implies larger values of  $J(\omega)$  in our analysis]. Also, a more recent assessment by Kihara *et al.*<sup>14</sup> of the distance of closest approach between molecular cores for a variety of cases including ethane from second virial coefficients has led to a value of 3.1 Å. This appears to be a more up-to-date result than the earlier estimate used by HM. Our results for the WT pcf are also shown in Fig. 4, and are seen to yield good agreement with experiment. Since for  $d=3.1$  Å we have  $\eta=0.2051$ , the Verlet correction is very small, only about 0.6% enhancement. We have not found it necessary to introduce any correction for finite jump, which, according to HM's analysis, would lead to a larger value of  $T_1^{-1}$ . [The analysis of finite jump diffusion with a reflecting B. C. at  $r=d$  has been discussed elsewhere<sup>5c</sup> along lines analogous to that of the Appendix. However, the existence of  $F(r) \neq 0$  results in a more ambiguous analysis, which may only be resolved with more microscopic analysis of the model.]

In recent work, we have pointed out the similarity in the formal results between a jump diffusion model and the Brownian diffusion model but with a frequency-dependent diffusion coefficient representing a memory effect.<sup>11</sup> We may note that incorporation of this effect into the calculation of the proton relaxation rate would lead to an increase in the magnitude of the (negative) slope of  $T_1^{-1}$  vs  $\omega^{1/2}$  (cf. Fig. 4). However, an analysis of this sort would only appear to be justified provided further  $T_1$  results at higher fields and frequencies are obtained.

Also, one would want to use a better pcf. In particular, HM used Hubbard's correction for off-center spins

yielding a 3% correction in the case of liquid ethane. Pcf's based on Lowden and Chandler's methods<sup>16</sup> are able to give intermolecular proton-proton pair-correlation functions for ethane rather than just the center of mass  $g(r)$ , and would therefore implicitly include such a correction.

## B. Ionic interactions

In a recent ESR and ENDOR study of spin relaxation of semiquinone radical ions, Leniart, Connor, and Freed<sup>17</sup> have suggested that differences in the concentration dependence of the ESR and ENDOR linewidths reflect, in part, contributions from the intermolecular electron-spin electron-spin dipolar interactions. Based partly on a simple argument from Torrey's theory and on the magnitude of the observed effects, these authors suggested that for a DH model the  $J(0)$  for uncharged species should be modified to  $(f^* e^{U(d)/kT})^{-1} J(0)$ , where

$$f^{*-1} \equiv d \int_d^\infty e^{U(r)/kT} dr/r^2. \quad (4.2)$$

A comparison between this suggestion and the results obtained in this work is given in Table II. It is found that the suggested form is a reasonable approximation, and is better for lower ionic strengths wherein the DH theory itself is a better approximation. We have not found a really satisfactory explanation for this convenient expression. Furthermore, it does not appear to lead to a correct and simple expression for the frequency dependence of  $J(\omega)$ .

Finally we note the availability of more reliable pcf's for ionic solutions than that from DH theory, which may be employed in the analysis of spin relaxation by translational diffusion.<sup>4</sup>

## APPENDIX A: ANALYTIC SOLUTIONS WHICH INCLUDE THE REFLECTING WALL BOUNDARY CONDITION AT $r=d$ .

One has, e. g., from Abragam,<sup>9</sup> that the conditional probability distribution for independent relative diffusion is

$$P(\mathbf{r} | \mathbf{r}_0, t) = \frac{1}{\sqrt{rr_0} 4\pi} \int_0^\infty e^{-Dt\rho^2} \rho d\rho \sum_L (2L+1) P_L(\cos\theta) \times J_{L+1/2}(\rho r) J_{L+1/2}(\rho r_0), \quad (A1)$$

TABLE II. Comparison of  $J(0)$  calculated for aqueous solutions of 1-1 electrolytes at 25 °C with the values of  $f^* e^{U(d)/kT}$  from Debye-Hückel theory.

Model <sup>a</sup>	$f^*$	$f^* e^{U(d)/kT}$	$J(0)^u/J(0)^b$
<i>Attraction</i>			
$I=0.0001$	2,288	0.418	0.436
$I=0.01$	1,963	0.407	0.370
<i>Repulsion</i>			
$I=0.01$	0,4550	2,137	1,853
$I=0.0001$	0,383	2,156	2,117

<sup>a</sup>Ionic strength in units of molarity.

<sup>b</sup> $J(0)^u$  represents the spectral density for uncharged molecules.

with  $J_{L+1/2}(\rho r)$  the Bessel function of order  $L + \frac{1}{2}$ . However, the correct conditional probability distribution requires a reflecting wall at  $r=d$ . The appropriate solution, in the notation of heat conduction, is given by Carslaw and Jaeger.<sup>18</sup> Here one merely replaces the  $J_{L+1/2}(\rho r)$  by  $F_{L+1/2}(\rho r)$  and  $J_{L+1/2}(\rho r_0)$  by  $F_{L+1/2}(\rho r_0)$ , where

$$F_{L+1/2}(\rho r) = \sqrt{\frac{2\rho r}{\pi}} \frac{[j_L(\rho r) y'_L(\rho d) - y_L(\rho r) j'_L(\rho r)]}{[j'_L(\rho d)^2 + y'_L(\rho d)^2]^{1/2}}, \quad (\text{A2})$$

where  $j_L(z)$  and  $y_L(z)$  are the spherical Bessel functions of the first and second kind, respectively, and of order  $L$ , and  $j'_L(z)$  and  $y'_L(z)$  are their derivatives. The two forms become identical when  $d \rightarrow 0$  (or more precisely,  $\rho d \rightarrow 0$ ).

Abraham<sup>9</sup> gives the correlation function for dipolar relaxation by independent relative diffusion as

$$G(t) = \pi \int_0^\infty \rho d \rho \exp(-Dt\rho^2) \left[ \int_0^\infty \frac{J_{5/2}(\rho r)}{r^{3/2}} dr \right]^2. \quad (\text{A3})$$

If, however, we employ the correct boundary condition at  $r=d$  and use Eqs. (A1)–(A2), then we must replace  $J_{5/2}(\rho r)$  by  $F_{5/2}(\rho r)$  in Eq. (A3), with

$$F_{5/2}(\rho r) = \sqrt{\frac{2\rho r}{\pi}} \frac{[j_2(\rho r) y'_2(\rho d) - j'_2(\rho d) y_2(\rho r)]}{[j'_2(\rho d)^2 + y'_2(\rho d)^2]^{1/2}}. \quad (\text{A4})$$

One then uses the well-known integrals of  $\int_d^\infty j_2(\rho r) dr/r^{3/2}$  and  $\int_d^\infty y_2(\rho r) dr/r^{3/2}$  as well as other standard properties of the spherical Bessel functions to obtain<sup>19</sup>

$$\int_d^\infty \frac{F_{5/2}(\rho r)}{r^{3/2}} dr = \sqrt{\frac{2\rho}{\pi}} \left( \frac{3}{\chi^3} \right) \left( \frac{81}{\chi^6} + \frac{9}{\chi^4} - \frac{2}{\chi^2} + 1 \right)^{-1/2}. \quad (\text{A5})$$

Then

$$G(t) = \frac{18\pi}{\pi d^3} \int_0^\infty e^{-t\chi^2/\tau} \frac{\chi^2 d\chi}{81 + 9\chi^2 - 2\chi^4 + \chi^6} \quad (\text{A6})$$

where we have introduced variables

$$\tau/t \equiv d^2/Dt, \quad (\text{A7a})$$

$$\chi \equiv \rho d. \quad (\text{A7b})$$

One method of solving Eq. (A6) is to break up the polynomial denominator into partial fractions. One first writes

$$\chi^6 - 2\chi^4 + 9\chi^2 + 81 = (\chi^2 + a)(\chi^2 + b)(\chi^2 + b^*), \quad (\text{A8})$$

where

$$a = 3.1800,$$

$$b = 2.5900 + i4.3318.$$

Then the partial fraction separation leads to the integrated form

$$G(t) = -\frac{9N}{d^3} [A\sqrt{a} e^{at/\tau} \operatorname{erfc}(\sqrt{at/\tau}) + B\sqrt{b} e^{bt/\tau} \times \operatorname{erfc}(\sqrt{bt/\tau}) + B^* \sqrt{b^*} e^{b^*t/\tau} \operatorname{erfc}(\sqrt{b^*t/\tau})], \quad (\text{A9})$$

where

$$B = \frac{i}{2} [(a-b) \operatorname{Im} b]^{-1} \quad (\text{A10a})$$

and

$$A = -B - B^* = -2 \operatorname{Re} B. \quad (\text{A10b})$$

We now let

$$J(\omega) = 2 \lim_{\epsilon \rightarrow 0^+} \operatorname{Re} \int_0^\infty G(t) e^{-(i\omega + \epsilon)t} dt, \quad (\text{A11})$$

where we have introduced the convergence term  $\epsilon \rightarrow 0^+$ . The transform given by Eqs. (A11) and (A9) is readily obtained,<sup>21</sup> as

$$J(\omega) = -2 \lim_{\epsilon \rightarrow 0} \operatorname{Re} \frac{9\pi}{d^3(s)^{1/2}} \left[ \frac{A\sqrt{a}}{\sqrt{s + \sqrt{a}/\tau}} + \frac{B\sqrt{b}}{\sqrt{s + \sqrt{b}/\tau}} + \frac{B^* \sqrt{b^*}}{\sqrt{s + \sqrt{b^*}/\tau}} \right] \quad (\text{A12})$$

where  $s = i\omega + \epsilon$ .

The bracketed terms in Eq. (A12) can be combined and rearranged, so that after some algebra one has

$$J(\omega) = \frac{18\pi}{d^3} \frac{\lim_{\epsilon \rightarrow 0} \operatorname{Re} \left[ \frac{1}{27} \tau^{-1/2} + \frac{1}{27} s^{1/2} \right]}{[9\tau^{-3/2} + 9\tau^{-1} s^{1/2} + 4\tau^{-1/2} s + s^{3/2}]} = \frac{8}{27} \frac{\pi}{Dd} \operatorname{Re} \left\{ [1 + \sigma'/4] / [1 + \sigma' + \frac{4}{3}\sigma'^2 + \frac{1}{3}\sigma'^3] \right\}, \quad (\text{A13})$$

where

$$\sigma \equiv (\omega\tau)^{1/2} = (\omega d^2/D)^{1/2}$$

and

$$\sigma' = i^{1/2} \sigma. \quad (\text{A14})$$

[One finds that the apparent discontinuity in Eq. (A12) for  $s=0$  is cancelled out once the bracketed term in Eq. (A12) is appropriately rearranged.] Equation (A13) is the general result for all frequencies  $\omega$ , and it is seen to have a rather simple form. In particular, to lowest power in  $\omega$  one has

$$J(\omega) \cong \frac{8}{27} \frac{\pi}{Dd} \left( 1 - \frac{3}{8} \sqrt{\omega d^2/D} \right). \quad (\text{A15})$$

The analytic solution to  $J(\omega)$  for the independent diffusion model is given by Hubbard<sup>8</sup> and is seen to involve transcendental functions of  $(\omega\tau)^{1/2}$ .

A related problem is that of relaxation through scalar spin-spin interactions as discussed in Abraham<sup>9</sup> and by Hubbard.<sup>8</sup> Hubbard studies the model of scalar interaction of finite but short range obeying

$$A(r) = \frac{Ad}{r} e^{-\lambda(r-d)}. \quad (\text{A16})$$

For this problem, one requires the correlation function

$$G_e(t) = 4\pi A^2 d^2 \pi C_e(t), \quad (\text{A17})$$

$$C_e(t) = \int_0^\infty \rho d \rho e^{-Dt\rho^2} \left\{ \int_d^\infty \exp[-\lambda(r-d)] J_{1/2}(\rho r) r^{1/2} dr \right\}^2 \quad (\text{A18})$$

in the independent diffusion model. Again we introduce the reflecting boundary condition at  $r=d$  by replacing  $J_{1/2}(z)$  by  $F_{1/2}(z)$  in Eq. (A18):

$$F_{1/2}(\rho r) = \sqrt{\frac{2}{\pi\rho r}} [1 + (\rho d)^{-2}]^{-1/2}$$

$$\times \left( \cos(r-d)\rho + \frac{\sin(r-d)\rho}{\rho d} \right). \quad (\text{A19})$$

One finds

$$\int_d^\infty \exp[-\lambda(r-d)] F_{1/2}(\rho r) r^{1/2} dr \\ = \sqrt{\frac{2d^3}{\pi\chi(1+\chi^2)}} \left( \frac{\gamma+1}{\gamma^2+\chi^2} \right), \quad (\text{A20})$$

where again  $\chi \equiv \rho d$  and  $\gamma \equiv \lambda d$ . Then

$$C_e(t) = \frac{2d}{\pi} \int_0^\infty e^{-t\chi^2/\tau} \frac{(\gamma+1)\chi^2 d\chi}{(1+\chi^2)(\gamma^2+\chi^2)^2}. \quad (\text{A21})$$

Again the denominator may be expanded by partial fractions, and the required integrations<sup>20</sup> performed to yield

$$C_e(t) = \frac{d}{(1-\gamma)^2} [\gamma e^{\gamma^2 t/\tau} \operatorname{erfc}(\gamma\sqrt{t/\tau}) - e^{t/\tau} \operatorname{erfc}(\sqrt{t/\tau})] \\ + \sqrt{\frac{2}{\pi}} \frac{2d}{\gamma} \left( \frac{1+\gamma}{1-\gamma} \right) e^{\gamma^2 t/2\tau} D_{-3}(\gamma\sqrt{2t/\tau}), \quad (\text{A22})$$

where  $D_{-n-1}(z)$  is a Whittaker or Parabolic Cylinder Function which is proportional to the  $n$ th repeated derivative (or integral) of  $\operatorname{erfc}z$ .<sup>19</sup> The Fourier transform of  $C_e(t)$  using the form Eq. (A11) is then found to be<sup>21</sup>

$$J_e(\omega) = \frac{8\pi A^2 d^5 \mathfrak{H}}{D} \left[ \frac{(1+\gamma)}{2\gamma^3(1-\gamma)} f\left(\frac{\sigma}{\gamma\sqrt{2}}, 1\right) - \frac{1}{\gamma(1-\gamma)} f\left(\frac{\sigma}{\gamma\sqrt{2}}, \gamma\right) \right], \quad (\text{A23})$$

where

$$f(z, \alpha) \equiv \frac{1+(1+\alpha)z}{1+2(1+\alpha)z+2(1+\alpha)^2 z^2+4\alpha(1+\alpha)z^3+4\alpha^2 z^4}. \quad (\text{A24})$$

Two special cases of this solution are, for  $\omega = 0$ ,

$$J_e(0) = \frac{8\pi A^2 d^2 \mathfrak{H}}{D\lambda^3} (\lambda d + \frac{1}{2}), \quad (\text{A25})$$

and for  $\gamma = \lambda d = 1$ ,

$$J_e(\omega) = \frac{12\pi A^2 d^5 \mathfrak{H}}{D} f\left(\frac{\sigma}{\sqrt{2}}, 1\right). \quad (\text{A26})$$

Equation (A25) appears to agree with the independent diffusion result of Hubbard<sup>8</sup> only for  $\lambda d \gg 1$ , because of the extra factor of  $\frac{1}{2}$ . However, a more careful analysis of the limit as  $\omega \rightarrow 0$  does show that the independent diffusion model also yields Eq. (A25). The general solution for  $J_e(\omega)$  for independent diffusion again involves transcendental functions. [Note Hubbard's  $J_e(\omega)$  is defined so as to equal  $\frac{1}{2}$  of our definition given in Eq. (A11).]

## APPENDIX B: THE REFLECTING WALL BOUNDARY CONDITION

One may write the Smoluchowski equation (2.3) with  $\mathbf{F}(r)$  separated into two parts, the hard-sphere (zero concentration) repulsive part, and the remaining contributions. The hard-sphere  $g(r)$  of Eq. (3.1) leads to  $U^{\text{HS}}(r) = \infty$  for  $r < d$ , which is the excluded volume effect, while  $U^{\text{HS}}(r) = 0$  for  $r > d$ , and to  $|F^{\text{HS}}(r)| = |F^{\text{HS}}| \delta(r-d + \epsilon)$ , where  $\epsilon$  is a positive infinitesimal ( $\delta$  is the Dirac delta function,) and  $|F^{\text{HS}}| \rightarrow \infty$ . Once the Smoluchowski

equation is written in this manner, we again apply the conservation of total probability given by Eq. (2.22a) and perform the integration of (2.22b) in the range  $d \leq r \leq \infty$  [in which  $F^{\text{HS}}(r) = 0$ ] to obtain

$$0 = \int_d^\infty d^3 r D \nabla \cdot [\nabla P - \mathbf{F}(r)P] = 4\pi d^2 D \left\{ -\frac{\partial}{\partial r} P + F(r)P \right\}_{r=d}, \quad (\text{B1})$$

where now  $F(r)$  excludes the hard-sphere component. Equation (B1) may be recognized as the reflecting wall boundary condition, and it is seen from the derivation to be physically equivalent to the conservation of total probability in the presence of a spherical excluded volume of radius  $d$ .

Finally we note that the Smoluchowski equation including  $F^{\text{HS}}(r)$ , when integrated over all space, does obey conservation of probability, as it should. Thus the use of the form of Eq. (2.8a) yields

$$\int d^3 r \frac{\partial P(\mathbf{r}, t)}{\partial t} \\ = -4\pi D \lim_{|F^{\text{HS}}| \rightarrow \infty} |F^{\text{HS}}| \int_0^\infty dr \frac{\partial}{\partial r} [\delta(r-d) r^2 P(\mathbf{r}, t)] = 0, \quad (\text{B2})$$

and we have used the fact  $\int_0^\infty \delta'(r-d) f(r) dr = -f'(r)|_{r=d}$ <sup>22</sup> to obtain the last equality before the limit  $F^{\text{HS}} \rightarrow \infty$  is taken (where the primes denote differentiation with respect to  $r$ ).

\*Supported in part by grants from the Petroleum Research Fund (Grant No. 6818-AC6) administered by the American Chemical Society, the National Science Foundation (Grant No. MPS75-00938), and by the Cornell University Materials Science Center.

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