

# Rotational diffusion coefficient of a rigid rod in a semidilute solution of spheres<sup>a)</sup>

R. Pecora and J. M. Deutch<sup>b)</sup>

Department of Chemistry, Stanford University, Stanford, California 94305

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Recently there has been considerable interest in the transport coefficients of rigid rod macromolecules in complex solution environments. In particular, Doi and Edwards<sup>1-3</sup> have presented a theory for the restricted rotational diffusion of a rigid rod of length  $L$  and diameter  $d$  in an isotropic solution of similar rods with number concentration  $n$  in the range  $1/L^3 \ll n \ll 2\pi/dL^2$ . For the rotational diffusion coefficient  $D_R$ , Doi and Edwards predict

$$D_R \propto kT \ln(L/d) / \eta_0 L^3 n^2, \quad (1)$$

where  $k$  is Boltzmann's constant,  $T$  is the absolute temperature, and  $\eta_0$  is the viscosity of the background solvent. The accuracy of this proposed relationship has been investigated experimentally<sup>4-6</sup> and by numerical simulations.<sup>7,8</sup>

Here we present an argument for the rotational diffusion coefficient of a rigid rod in a solution which contains rigid spheres of radius  $R$  at number concentration  $n$ . Our result is

$$D_R \propto kT / \eta_0 L^4 R n^{2/3}, \quad (2)$$

which should be compared to the dilute solution result<sup>9,10</sup>  $D_R \propto kT \ln(L/d) / \eta_0 L^3$  and the Doi-Edwards prediction, Eq. (1). The rotational diffusion coefficient of a rigid rod immersed in spheres will exhibit a weaker dependence on rod length and concentration than a rigid rod immersed in other rods.

Our theoretical argument for this result is based on the same physical picture adopted by Doi and Edwards. We imagine that the rod is trapped by the hard cores of neighboring spheres and restricted to rotational displacements  $\Delta s$

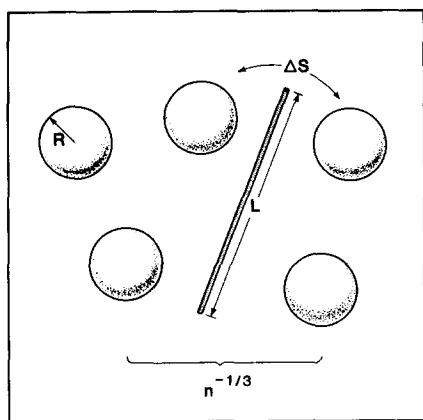


FIG. 1. A rigid rod of length  $L$  trapped by surrounding spheres of radius  $R$  which have an average separation  $n^{-1/3}$ . For a fixed arrangement of the spheres, the rod can rotate through an arc length  $\Delta s$ .

or angular displacements  $\Delta\theta = \Delta s/L$  for the time period  $t$  during which the environment of surrounding spheres remains steady; see Fig. 1. The rotational diffusion coefficient is determined from the equation

$$D_R = (\Delta\theta)^2 / t \quad (3)$$

and  $\Delta s$  is estimated to be proportional to the average distance between spheres,  $\Delta s \propto n^{-1/3}$ . The relaxation time  $t$  is estimated by the time required for a sphere to diffuse away from the rod according to  $L^2 \propto D_s t$ , where  $D_s$  is the translational self-diffusion coefficient for a sphere. Combining these results leads to

$$D_R \propto D_s / L^4 n^{2/3}. \quad (4)$$

According to Stokes law, in dilute solutions,  $D_s \propto kT / \eta_0 R$  and one arrives at our central result, Eq. (2). The limits of applicability of our argument are: (a) the rods and spheres are of comparable size  $L \sim R$  (although the spheres must be somewhat smaller than the rods); (b) the concentration of spheres is sufficiently high for some caging to occur  $2\pi > (Ln^{1/3})^{-1}$ , but not so high that there is significant overlap among the spheres ( $R^3 n < 1$ ).

Our result, Eq. (2), may be extended in a number of ways. First, if we assume that the spheres are nonfree draining polymer molecules with structure  $R \sim N^\nu$ , where  $N$  is the number of segments in each polymer molecule, Eq. (2) leads to the prediction for the molecular weight dependence of the rod rotational diffusion coefficient  $D_R \propto N^{-\nu}$ .

Second, one may imagine that the spheres are immobile and form a rigid gel-like network with an average distance between entanglement points given by  $p \sim n^{-1/3}$ . In this case, the relaxation time is determined by the motion of the rod itself and  $D_s$  in Eq. (4) must be replaced by the translational diffusion coefficient of the rod<sup>9,10</sup>  $D_T \propto kT \ln(L/d) / \eta_0 L$ . One predicts

$$D_R \propto p^2 kT \ln(L/d) / \eta_0 L^5 \quad (5)$$

in agreement with the result given by de Gennes.<sup>11</sup>

Third, it should be noted that it is possible to replace the Stokes law value for the translational diffusion coefficient of a sphere by a value appropriate to a finite concentration. In this concentration regime we might conjecture  $D_s(\phi) = D_s^0 [\eta_0 / \eta(\phi)]$ , where  $\phi$  is the volume fraction of spheres in the solution. Thus, more generally, Eq. (2) should be  $D_R \propto kT / \eta(\phi) L^4 R n^{2/3}$ .

In summary, we have presented a theoretical argument based on hard core caging for the dependence of the rotational diffusion coefficient of a rigid rod immersed in a solution of spheres. This model should prove useful for the interpretation of polymer solution behavior.

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- <sup>b</sup>On leave from the department of Chemistry, M.I.T.; J. M. D. thanks the Department of Chemistry at Stanford University for its hospitality.
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## ERRATA

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**Erratum: MS- $\chi\alpha$  calculation of the elastic electron scattering cross sections and x-ray absorption spectra of CX<sub>4</sub> and SiX<sub>4</sub> (X = H, F, Cl) [J. Chem. Phys. **80**, 813 (1984)]**

J. A. Tossell and J. W. Davenport

*Departments of Chemistry and Biochemistry, The University of Maryland, College Park, Maryland, 20742*

The elastic electron scattering cross sections shown in Figs. 2–7 are *too large* by a *factor of 2* due to our failure to require that the spin projection quantum number of the scattering electron be conserved. Also, in Table I the oscillator strength for the Si2p→t<sub>2</sub> excitation in SiF<sub>4</sub> should be 0.000 97.