EFFECT OF IMPINGEMENT ON THE ROTATIONAL DIFFUSION COEFFICIENT OF RIGID RODS

Andrzej Ziabicki

Polish Academy of Sciences, Institute of Fundamental Technological Research,
ul. Swietokrzyska 21, PL-00-049 WARSAW, Poland

In a series of papers concerned with dynamics of concentrated solutions of rigid, rodlike macromolecules, Doi and Edwards [1-3] introduced effects of rod impingement on the rotational motions. The result obtained for a rod with orientation u with respect to the fixed coordinate system was:

$$D_r(\theta)/D_{ro} = \beta/[2\pi cL^3 \int \Psi(\theta')|\sin(\theta,\theta')|\ \sin\theta'\ d\theta']^2 \qquad (1)$$

where D_{ro} denotes unperturbed diffusion coefficient, $\Psi(\theta)$ is orientation distribution function, c - average number density of rods in the solution, and L - their length. In the original treatment β was assumed a dimensionless constant of the order of unity; however, numerical simulation [4] and experimental data [5,6,8-11] yield β higher by 2-4 orders of magnitude, i.e. rotational diffusivities much higher than predicted by Doi and Edwards

The main assumptions on which the original model has been constructed can be summarized as follows: - in a dense system, motions of the rods are confined to axial translation and libration within a "tube"

with radius a. Rotational freedom is characterized by the ratio a/L, and the rotational diffusion coefficient, D_r divided by the unperturbed value, D_{ro}, reads

$$D_r/D_{ro} = (a/L)^2 \qquad (2)$$

The key role in the model is played by the density of impingements, i.e. the number of rods intersecting surroundings of the considered rod. The average number of intersections of the surface of a cylinder of length L, and radius r, oriented at the angle θ with respect to the fixed coordinate system, reads [1-3]:

$$N(r,\theta) = 2\pi crL^2 \int \Psi(\theta')|\sin(\theta,\theta')|\ \sin\theta' d\theta' =$$

$$= 2\pi cL^2 <|\sin(\theta,\theta')|> \qquad (3)$$

The radius, a, of the constraining "tube" is found from an arbitrary assumption that the average number of impingements on the tube surface, is equal to unity, which yields:

$$a = 1/2\pi cL^2 <|\sin(\theta,\theta'|> \qquad (4)$$

Since eq.(2) with a from eq.(4) does not fit experimental data, the resulting diffusion coefficient is generally multiplied by a correction coefficient, β, yielding eq.(1).

Eq.(1) has several shortcomings. First, it is not applicable to dilute solutions, leading to infinite mobility at c=0. Doi and Edwards did not propose their model to describe systems with *average* inter-particle distance smaller than L, but local fluctuations of concentra-

tion can produce impingement effects at any, arbitrarily small concentrations. Infinite rotational mobility is also predicted when the system is ideally oriented, i.e. when $\Psi(\theta) = \delta(\theta)$. Intuitively, one would expect impingements to reduce diffusion coefficient, but never to increase it above the unperturbed level, D_{ro}. Only in the limit of c=0, or ideally oriented system, asymptotic value of the diffusion coefficient should approach D_{ro}, characteristic of an isolated rod. Last, not least, the correction coefficient β should be interpreted. The necessity of introduction of a large coefficients β suggests that the impingements are much less effective than assumed in the original "tube" considerations or, that one intersection per cylinder surface does not define an effective "tube". The Doi-Edwards formula has been criticized by many authors, who either suggested refinement of the "tube" (or "cage") model [5-7] or proposed alternative solution of the problem [8]. In this paper we shall try to reinterpret assumptions of the Doi-Edwards model and make it applicable in the entire range of concentrations and orientations. Applicability of the model is still to be proved by more thorough experimental and simulation tests.

Instead of postulating an "average tube" with an *a priori* defined radius a, (eq. 4), and then correcting the final result with an arbitrary multiplier β, we shall assume, that the "effective tube" has an unknown radius to be determined empirically. Eq.(2) will now be written as:

$$D_r/D_{ro} = (a_{eff}/L)^2 = \beta(a/L)^2 \qquad (5)$$

Identifying a_{eff} with $a\sqrt{\beta}$, where a is the original (Doi-Edwards) tube radius, and β - the correction coefficient, we arrive directly at eq.(1). Eq. (5) corresponds to $N=\sqrt{\beta}$ intersections (impingements) on the surface of an "effective tube", rather than one assumed in eq.(4). It may be noted that the reduced diffusion coefficient, Eq.(2a) can be expressed through the number of impingements on the surface of another, "interaction tube" with radius $R=L/\sqrt{\beta}$

$$D_r(\theta)/D_{ro} = 1/[N(R,\theta)]^2 \qquad (6)$$

Equation (6) leads to the same result as the "adjusted" Doi-Edwards theory (eq.1). What it describes is the situation in which each rod is surrounded by the same (average) number of other rods, and yield physically sensible results only when the number of impingements on the surface of the "interaction tube" is larger than unity. This is true for large concentrations and rod lengths (cL^3) and small degrees of orientation (not too small values of $\langle|\sin(\theta,\theta')|\rangle$. To account for situations involving arbitrary concentrations and orientations, we shall consider *local* (rather than *average*) number of impingements on the surface of the "interaction tube", n, subject to probability distribution, P(n). The average number, $\langle n\rangle = N(R,\theta)$, is equal to that in the original Doi-Edwards model, but, even at very low *average* concentrations there is a finite probability of impingement, and the overall diffusion coefficient is reduced. Instead of eqs. (2) or (6) we consider harmonic average of the diffusion coefficient over the impingement-number distribution P(n). Harmonic average appears because *rotation time*, not *rotation velocity* is additive.

$$D_{ro}/D_r = \sum_{n=0}^{\infty} P(n)\, F(n) \tag{7}$$

The weight function, is assumed in the form

$$F(n) = \begin{cases} 1 & \text{for } n=0 \\ n^2 & \text{for } n>0 \end{cases} \tag{8}$$

Whenever in the vicinity of the test rod (r=R) no other rods are present (n=0), the diffusion coefficient is unchanged ($D_r = D_{ro}$). When other rods are encountered (n>0), diffusion time increases as n^2, and D_r decreases as n^{-2}, as in the original Doi-Edwards model. The probability distribution is normalized

$$\sum_{n=0}^{\infty} P(n) = 1 \tag{9}$$

and the first moment is equal to the number of impingements appearing in the original model

$$\sum_{n=0}^{\infty} n\, P(n) = N(R,\theta) \tag{10}$$

Assuming that P(n) is represented by the Poisson distribution

$$P(n) = e^{-N} N^n/n! \tag{11}$$

one obtains

$$D_r/D_{ro} = 1/[e^{-N} + N + N^2] \tag{12}$$

In the range of high impingement concentrations, eq.(10) asymptotically approaches the original result of Doi and Edwards. At $N(R,\theta)=0$, i.e. for infinitely diluted, or ideally oriented systems, D_r reduces to unperturbed diffusion coefficient D_{ro}. The ratio D_r/D_{ro} never exceeds the range (0,1), and monotonically decreases with increasing density of impingements. It may be noted that also simpler expression

$$D_r/D_{ro} \simeq 1/[1 + N^2] \qquad (12a)$$

preserving all basic features of the more complete formula (12) approximates well the rotational diffusion ratio D_r/D_{ro} in the entire range of variables. Eq. (12a) can be obtained by "sewing" the two asymptotic forms of eq. (12) for very small, and very large N. Its maximum error of the approximation (12a) with respect to (12) amounts to 23.8% at N=1.85. On the other hand, diffusion coefficients calculated from the unmodified Doi-Edwards theory, at small concentrations are much larger than D_{ro} (infinite at N=0), and their error with respect to eq. (12) drops below 25% only above N=4. The corresponding relations are illustrated in Figure 1. Our equations (12,12a), as well as the "adjusted" Doi-Edwards formula (6) include an unknown parameter, β. To test all results, we have plotted in Figure 2 $\log(D_r/D_{ro})$ for a randomly oriented system ($\langle|\sin(\theta,\theta')|\rangle=\pi/4$) vs. concentration parameter, $\log(cL^3)$. The points represent data from the Monte Carlo simulation by Doi, Yamamoto and Kano [4]. It is evident that our formulae (12,12a) yield a reasonably good fit in the entire range of the single variable cL^3 when the parameter is assumed as $(4\beta/\pi^4)=540$. The same value was used by Doi et coll. [4] for fitting

asymptotic behavior of their formula at high concentrations. The unextended Doi-Edwards formula (6) can be fit to the data only for cL^3 larger than 60.

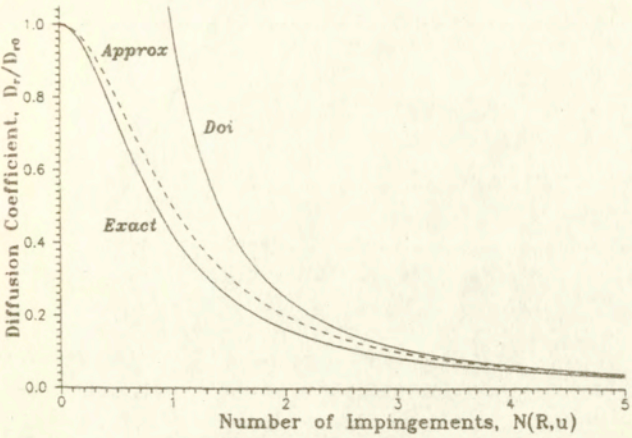

Figure 1.

Reduced rotational diffusion coefficient, D_r/D_{ro}, for a system of rigid rods vs. average number of impingements on the surface of an "interaction tube", N(R). *Exact* - eq.(12), *Approx* - eq.(12a), *Doi* - eq.(6).

There is one more simplification which can be introduced into the Doi-Edwards orientation-dependent diffusion coefficient (eqs. 1 and 3). Replacing square of the average absolute sine, by the average sine square we arrive at the rotational diffusion coefficient D_r in the form

$$D_r/D_{ro} = 1/[1 + a(cL^3)^2\langle\sin^2(\theta,\theta')\rangle] \qquad (13)$$

which can be easily integrated with various orientation functions $\Psi(\theta)$.

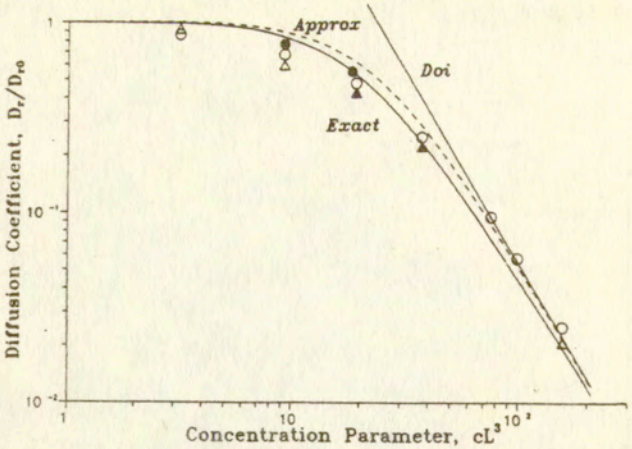

Figure 2.

Reduced rotational diffusion coefficient, D_{r_3}/D_{ro}, for a system of rigid rods vs. average concentration, cL^3. Assumed parameter: $(4\beta/\pi^4)=540$. *Exact* - eq.(12), *Approx* - eq.(12a), *Doi* - eq.(6). Points represent various sets of Monte Carlo experiments by Doi et coll. [4].

To investigate the error introduced by such replacement, we have calculated $\langle|\sin\theta|\rangle^2$ and $\langle\sin^2\theta\rangle$ and the relative error for a wide range of average orientations characterized by the second Legendre function $\langle P_2\rangle = (3\langle\cos^2\theta\rangle-1)/2$. The distribution function used

$$\Psi(\theta) = \text{const.}\ \exp(A^2\cos^2\theta) \qquad (14)$$

covers the entire range of average orientations from a random system ($A^2=0$, $\langle P_2\rangle=0$) to ideal parallelization of all rods ($A^2=\infty$, $\langle P_2\rangle=1$). The asymptotic values can be calculated easily and yield

	$\langle\lvert\sin\theta\rvert\rangle$	$\langle\sin^2\theta\rangle$	error, Δ
unoriented $\langle P_2\rangle=0$	$\pi/4$	2/3	0.050
$\langle P_2\rangle_{max} = 0.338$	0.612	0.441	0.067
fully oriented $\langle P_2\rangle=1$	0.000	0.000	0.000

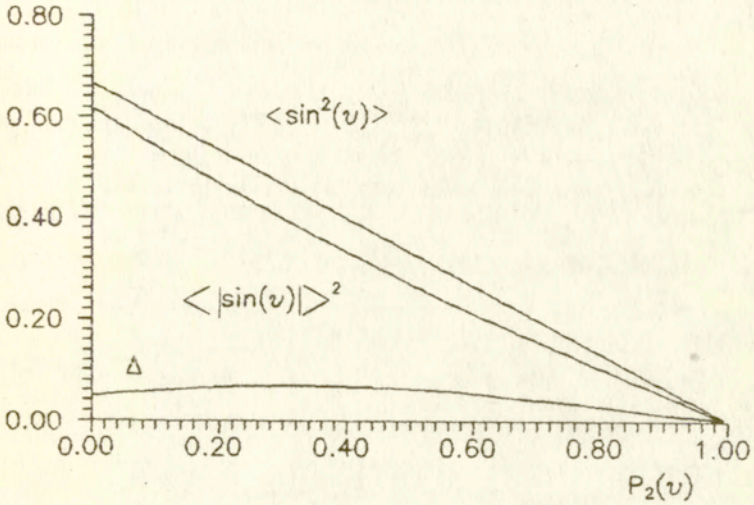

Figure 3.

Square of the average absolute sine, average sine square and their difference, Δ, as a function of the average degree of orientation, $\langle P_2\rangle = (3\langle\cos^2\theta\rangle-1)/2$.

The data presented in Figure 3 show that the error associated with the approximation, $\Delta = (\langle\sin^2\theta\rangle-\langle\lvert\sin\theta\rvert\rangle^2)$ initially increases with orientation, assumes a maximum, and gradually decreases to zero at high orientations. Replacement of the square of average absolute sine by

average sine square does not change the general character or symmetry of the characteristics and greatly facilitates analytical solutions of problems involving orientation-dependent diffusion coefficient.

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