with Bessel function

$$K_0(z) = \int_0^\infty \frac{e^{-z(x^2+1)^{1/2}}\,dx}{(x^2+1)^{1/2}} \tag{15}$$

which for small z becomes

$$z = -\ln z + \ln 2 - \gamma + \mathcal{O}(z^2 \ln z) \tag{16}$$

Finally we employ Brinkman's reasoning[4] to obtain ξ. In eq 1 the macroscopic flow is dominated by the screening term so that the pressure difference Δp on a column of the suspension of length l and cross-section A is given by Darcy's law

$$\Delta p/l = \eta_0 v_0/\xi^2 \tag{17}$$

where v_0 is the average fluid velocity with respect to the rods. Hence, the total force on the particles enclosed in volume $V = Al$ is

$$A\Delta p = V\eta_0 v_0/\xi^2 \tag{18}$$

The total force exerted on the N rods in the same volume can also be calculated with the help of eq 10 and 14

$$A\Delta p = 3\pi\eta_0 L v_0 N K_0^{-1}(a/\xi) \tag{19}$$

Self-consistency demands that

$$K_0(a/\xi)\xi^{-2} = 3\pi cL \tag{20}$$

where we have introduced the number density $c = N/V$. The friction coefficient for $a \ll \xi \ll L$ becomes

$$\Xi = \frac{3\pi\eta_0 L}{\ln(\xi/a) + \ln 2 - \gamma} \tag{21}$$

Equation 20 is all but identical to the result of ref 1. The slight disparity would disappear if one were to use the same short-distance cut-offs.

Several comments on the validity of these calculations are in order. As in ref 1 we have assumed the background is a uniform, isotropic medium acting on the probe only hydrodynamically and not mechanically. Taking the coupling between rods along would modify the numerical coefficients in eq 13 and 21. Note that there is some numerical evidence[3] that rods in semidilute solutions may overlap substantially with only minor entanglement.

Another difficulty is the nature of hydrodynamic screening. This seems plausible for a particle diffusing through a fixed network, the perturbed fluid being slowed down by the network just as it is by walls of a vessel in Poiseuille flow.[18,19] The existence of hydrodynamic screening for swarms of moving particles is often doubted. Brinkman[4] simply wrote down eq 1 ad hoc. Freed and Edwards[5] developed an elaborate though still not rigorous theory in which they replaced a complicated tensor depending on many-particle interactions by an averaged one. Finally, Lekkerkerker and Bedeaux[20] have pointed out that the interpretation of eq 1 may be difficult because the amount of screening depends on the reference frame since eq 1 is not Galilean invariant. This problem does not arise here because the noninvariant terms are of the same order as those deleted in the slender-body approximation.

In summary, these calculations could be useful for a rod moving through a gel or through a swarm of much longer rods (which can be considered fixed on the diffusion time scale of the probe rod) as long as mechanical entanglement can be assumed negligible. The application to other cases (e.g., all rods of equal length) is speculative and probably much more approximate.

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References and Notes

(1) Muthukumar, M.; Edwards, S. F. *Macromolecules* **1983**, *16*, 1475.
(2) Doi, M. *J. Phys. (Les Ulis, Fr.)* **1975**, *36*, 607.
(3) Keep, G. T.; Pecora, R. *Macromolecules* **1985**, *18*, 1167.
(4) Brinkman, H. C. *Appl. Sci. Res.* **1947**, *A1*, 27.
(5) Freed, K. F.; Edwards, S. F. *J. Chem. Phys.* **1974**, *61*, 3626.
(6) Yamakawa, H.; Fujii, M. *Macromolecules* **1973**, *6*, 407.
(7) Burgers, J. M. *Second Report on Viscosity and Plasticity of the Amsterdam Academy of Sciences*; Nordemann: New York, 1938.
(8) Broersma, S. *J. Chem. Phys.* **1960**, *32*, 1632.
(9) Taylor, G. *Proc. Roy. Soc. London, A* **1951**, *A209*, 407.
(10) Hancock, G. J. *Proc. Roy. Soc. London, A* **1953**, *A217*, 96.
(11) Batchelor, G. K. *J. Fluid Mech.* **1970**, *44*, 419.
(12) Lighthill, J. *SIAM Rev.* **1976**, *18*, 161.
(13) Lighthill, J. *Mathematical Biofluiddynamics*; Society for Industrial and Applied Mathematics: Philadelphia, 1975.
(14) Stockmayer, W. H. In *Molecular Fluids*; Balian, R., Weill, G., Eds.; Gordon and Breach: London, 1976.
(15) Fixman, M. *J. Chem. Phys.* **1982**, *76*, 6124.
(16) Fixman, M. *J. Chem. Phys.* **1983**, *78*, 1588.
(17) Chambers, L. G. *Integral Equations—A Short Course*; International Textbook: East Kilbride, Scotland, 1976; Chapter 5.
(18) Batchelor, G. K. *Annu. Rev. Fluid Mech.* **1974**, *6*, 227.
(19) Batchelor, G. K. *An Introduction to Fluid Dynamics*; Cambridge University Press: Cambridge, Great Britain, 1967.
(20) Lekkerkerker, H. N. W.; Bedeaux, D., private communication.

Comparison of Predicted Rouse-Zimm Dynamics with Observations for a 2311 Base Pair DNA Fragment

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In this work we use estimates of the radius of gyration and the translational diffusion constant of a 2311 base pair (bp) DNA fragment (1.53×10^6 molecular weight)[1] in solution to calculate the decay times predicted by the Rouse–Zimm model[2,3] for a flexible polymer. These calculations, when combined with previous electric birefringence measurements,[4] allow us to determine the degree to which the dynamics of this DNA fragment fit the predictions of the Rouse–Zimm model.

Radius of Gyration and Translational Diffusion Constant

Assuming a rise per base pair of 3.36 Å[5] the contour length of the 2311-bp DNA fragment would be 7760 Å. We will assume that the effects of excluded volume may be neglected for a DNA of this length and use a well-known formula for the radius of gyration of a wormlike coil[6]

$$R_g^2 = \frac{LP}{3} - P^2 + \frac{2P^3}{L} - \frac{2P^4}{L^2}(1 - e^{-L/P}) \tag{1}$$

where L is the contour length of the molecule and P is the persistence length. Many different measurements have been made of the persistence length of DNA in both high- and low-ionic-strength buffers[7-11] and the reported values show some variation. We will assume the persistence length in high-ionic-strength buffer (containing 100 mM Na^+) to be 500 Å. Although we note that there is some disagreement in the literature over the effect of ionic strength on the persistence length,[7-12] we will follow the recent work of Cairney and Harrington[8] and assume the persistence length to be 1000 Å in the low-ionic-strength buffer used for electric birefringence measurements.[4] Using these values in eq 1, we would predict a radius of

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Table I
Measured and Predicted Translational Diffusion Constants (cm^2/s)

measured translational diffusion constant (1 mM $NaPO_4$)	$(3.16 \pm 0.13) \times 10^{-8}$
measured translational diffusion constant (1 mM $NaPO_4$, 100 mM NaCl)	$(3.83 \pm 0.17) \times 10^{-8}$
prediction from sedimentation	3.76×10^{-8}

gyration of 1030 Å in the higher ionic strength buffer and 1350 Å in the lower ionic strength buffer. As a simple check of these estimates we have performed classical light scattering measurements on this DNA in high-ionic-strength buffer,[13] obtaining a radius of gyration of 1040 Å, in good agreement with the first estimate.

Although, as detailed in previous work,[14] we may use sedimentation results to estimate the translational diffusion constant for our DNA, the sedimentation work[15] was carried out in buffers containing 0.195 M Na^+. In order to obtain a translational diffusion constant valid under low-ionic-strength conditions we have performed several dynamic light scattering experiments[16] using standard techniques.[13] The results of these experiments and the comparison with the sedimentation prediction are shown in Table I. As expected, the measured diffusion constant in high-ionic-strength buffer agrees with the sedimentation prediction. In the low-ionic-strength buffer the diffusion constant is slightly smaller. Using the values for the radius of gyration and the translational diffusion constant of the DNA in the buffer used for the transient electric birefringence experiments, we may now proceed to predict the Rouse–Zimm decay times.

Prediction of the Rouse–Zimm Decay Times

The Rouse–Zimm model[2,3] predicts the frequencies and motions of the normal modes that are expected for an infinitely flexible molecule. In its basic form, the model either disregards the hydrodynamic interactions between different sections of the molecule (the so-called free-draining limit) or it assumes that these interactions are limiting the dynamics (the so-called non-free-draining limit).

In the free-draining limit the relaxation times of the internal modes may be expressed in terms of the radius of gyration of the molecule and the translational diffusion constant. This is shown in Berne and Pecora,[16] but the time that they derive is twice the time that Zimm[2] originally called τ_κ. The expression for the Zimm times in the free-draining limit is

$$\tau_\kappa = R_g^2/\pi^2 D\kappa^2 \qquad (2)$$

where R_g is the radius of gyration, D is the translational diffusion constant, and κ is the mode number. In the non-free-draining limit the expression for the relaxation times of the normal modes is[2,3]

$$\tau_\kappa = 11.8\eta R_g^3/kT\lambda_\kappa' \qquad (3)$$

where η is the solvent viscosity, k is Boltzmann's constant, T is the absolute temperature, and λ_κ' is an eigenvalue given in ref 3. Stockmayer and Baur have shown that the τ_κ are the times expected in the birefringence decay.[17]

If we choose the number, size, and spacing of the beads in the Rouse–Zimm model so that we match the contour length, radius of gyration, and the free-draining translational diffusion constant of our DNA in the low-ionic-strength buffer, our model would consist of 10 beads of radius 6.8 nm connected by bonds of average length 86 nm. These values give a draining parameter,[2] h, of 0.23. The free-draining limit corresponds to $h \ll 1$ and the non-free-draining limit to $h \gg 1$. Thus these parameters for our DNA would suggest that we should expect behavior closer to the free-draining limit than the non-free-draining limit.

Table II
Predicted Decay Times of Rouse–Zimm Modes (μs)[a]

mode no.	free-draining limit	non-free-draining limit	obsd
1	584	1780	688
2	146	561	204
3	65	297	40–60

[a] $R_g = 1.35 \times 10^{-5}$ cm; $D = 3.16 \times 10^{-8}$ cm^2/s.

Comparison of Transient Electric Birefringence Data with the Rouse–Zimm Predictions

Using our estimates for the radius of gyration and the translational diffusion constant under the conditions of the transient electric birefringence experiments and using eq 2 and 3, we obtain the decay times shown in Table II. The times observed by the birefringence experiments[4] are shown for comparison.

The free-draining limit of the Rouse–Zimm model comes surprisingly close to predicting the positions of the first three relaxations observed in the DNA. As noted in our previous work[4] different models, appropriate for shorter DNA fragments, predict ratios of decay times inconsistent with the data from the 2311-bp fragment. There are several reasons to be surprised that the Rouse–Zimm model fits the observations on the 2311-bp DNA so well. First of all, the DNA is not infinitely flexible as the Rouse–Zimm model assumes but is in fact rather stiff with a persistence length probably of approximately 1000 Å. Secondly, the free-draining limit ignores the hydrodynamic interactions between the different sections of the molecule. While it is possible that these oversimplifications fortuitously canceled each other, these observations suggest that the simple Rouse–Zimm model does rather well in describing the dynamics of this semistiff macromolecule.

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References and Notes

(1) Lewis, R. J.; Huang, J. H.; Pecora, R. *Macromolecules* **1985**, *18*, 1530.
(2) Zimm, B. H. *J. Chem. Phys.* **1956**, *24*(2), 269.
(3) Zimm, B. H.; Roe, G. M.; Epstein, L. F. *J. Chem. Phys.* **1956**, *24*(2), 279.
(4) Lewis, R. J.; Pecora, R.; Eden, D. *Macromolecules* **1986**, *19*, 134.
(5) Dickerson, R. E. *Sci. Am.* **1983**, *249*(6), 94.
(6) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971; p 56.
(7) Harrington, R. E. *Biopolymers* **1978**, *17*, 919.
(8) Cairney, K. L.; Harrington, R. E. *Biopolymers* **1982**, *21*, 923.
(9) Borochov, N.; Eisenberg, H.; Kam, Z. *Biopolymers* **1981**, *20*, 231.
(10) Kam, Z.; Borochov, N.; Eisenberg, H. *Biopolymers* **1981**, *20*, 2671.
(11) Rizzo, V.; Schellman, J. *Biopolymers* **1981**, *20*, 2143.
(12) Mandel, M.; Schouten, J. *Macromolecules* **1980**, *13*, 1247.
(13) Lewis, R. J. Ph.D. Thesis, Stanford University, Stanford, CA, 1985.
(14) Lewis, R. J.; Huang, J. H.; Pecora, R. *Macromolecules* **1985**, *18*, 944.
(15) Kovacic, R. T.; van Holde, K. E. *Biochemistry* **1977**, *16*(7), 1490.
(16) Berne, B. J., Pecora, R. "Dynamic Light Scattering"; Wiley: New York, 1976.
(17) Stockmayer, W. H.; Baur, M. E. *J. Am. Chem. Soc.* **1964**, *86*, 3485.