(46) Frauenfelder, H.; Petsko, G. A.; Tsernoglou, D. *Nature (London)* **1979**, *280*, 558.
(47) Artymiuk, P. J.; Blake, C. C. F.; Grace, D. E. P.; Oatley, S. J.; Phillips, D. C.; Sternberg, M. J. E. *Nature (London)* **1979**, *280*, 563.
(48) Skolnick, J.; Helfand, E. *J. Chem. Phys.* **1980**, *72*, 5489.
(49) Helfand, E.; Wasserman, Z. R.; Weber, T. A.; Skolnick, J.; Runnels, J. H. *J. Chem. Phys.* **1981**, *75*, 4441.
(50) Evans, G. T.; Knauss, D. C. *J. Chem. Phys.* **1980**, *72*, 1504.
(51) Knauss, D. C.; Evans, G. T. *J. Chem. Phys.* **1981**, *74*, 4621.

Hydrodynamic Properties of a Torsionally Flexible Cylinder: An Application to DNA

Stuart A. Allison

Institute of Molecular Biology, University of Oregon, Eugene, Oregon 97403.

Received February 16, 1982

ABSTRACT: The hydrodynamic properties of a torsionally flexible cylinder are studied using the extrapolated shell method. The method appears to be exact. What is derived is a general equation that relates the angular velocity at some point along the cylinder to the torque per unit length acting on the entire cylinder. In the special case of a torque that varies sinusoidally along the cylinder, a simple equation for the rotational friction coefficient is derived. This result is important in connection with the dynamical theory of torsion in macromolecules in which only approximate account of hydrodynamic interaction has been taken to date. In the case of DNA, it is concluded that present theory is valid down to approximately 5 ns and that by taking hydrodynamic interaction properly into account, theory would be valid down to about 0.1 ns.

Introduction

In this article, the hydrodynamic properties of a long cylinder that is torsionally flexible are considered. Specifically, a general equation is derived relating the instantaneous angular velocity at some point to the instantaneous torque per unit length acting over the entire cylinder. This result appears to be exact within the limitations of the assumptions about the nature of the fluid and its interaction with the cylinder surface. In the special case of a long cylinder undergoing uniform rotation about the cylindrical axis, Perrin's result is obtained[1]

$$\tau_{\text{hydro}} = \gamma_{\text{P}}\omega \tag{1}$$

$$\gamma_{\text{P}} = 4\pi\eta a^2 \tag{2}$$

where τ_{hydro} is the hydrodynamic torque per unit length, ω is the angular velocity, γ_{P} is the rotational friction coefficient per unit length, η is the solvent viscosity, and a is the radius of the cylinder.

This work was motivated by the recent interest in the rapid twisting or torsional motions of DNA detected by fluorescence depolarization[2–4] and EPR.[5] The dynamical theory of DNA twisting was originally worked out independently by Barkley and Zimm[6] and Allison and Schurr.[7] Since then, the effect of torsional motions on NMR relaxation parameters[8] and depolarized light scattering[9] have been studied. It can be anticipated that torsional motions in macromolecules will be the subject of numerous future investigations.

To date, the hydrodynamic interactions of a torsionally flexible macromolecule have only been accounted for in an approximate way. Both Barkley and Zimm[6] and Allison and Schurr[7] used the Perrin formula (eq 1) to account for the hydrodynamic torque. In any dynamical model, this is exact only if the entire molecule (modeled as a cylinder) rotates at the same rate. If, for example, a small region of the cylinder rotates faster than neighboring regions at a given instant, then the hydrodynamic torque on the faster moving region would be larger than predicted using the Perrin formula because of increased solvent drag. One of the primary objectives of this work is to account more accurately for the hydrodynamic interactions in a dynamical model of macromolecular torsion.

The problem is approached using the extrapolated shell method.[10,11] This method originated with Bloomfield et al.[12] and consists basically of viewing the hydrodynamic properties of the macromolecule as resulting from the solvent perturbation by point sources of friction uniformly distributed over the object's surface. The problem of the hydrodynamic interaction between point sources of friction was considered by Oseen,[13] who derived an interaction tensor, the Oseen tensor, for any configuration. This tensor has been extended to account for the finite size of the (spherical) beads and is known as the modified Oseen tensor in this form.[14,15]

The macromolecule is modeled by placing a large number of identical beads uniformly over its surface and the hydrodynamic properties (translational and rotational friction coefficients) are determined using the Oseen tensor or its modified form. In general, the problem must be solved numerically for a finite number of beads. The process is repeated using a larger number of smaller beads and finally, the limit of an infinite number of beads of infinitesimal size is estimated by extrapolation.[10,11] In this limit, the shell model appears to be exact and is of great value and utility since it can, in principle, be applied to macromolecules of any geometry. Unfortunately, these calculations are expensive and time-consuming. Garcia de la Torre and Bloomfield have described various approximations and possible alternatives to the extrapolated shell method.[16,17]

In a few limited cases where the object possesses a high degree of symmetry, it is possible to solve the problem analytically. A still broader class of problems can be solved analytically if, for example, use is made of the Kirkwood approximation.[18] Recently, the translational friction of a toroid was solved in this manner and was found to be accurate to within a few percent of the exact value.[19] (In the case of the toroid, the exact value was determined numerically by the extrapolated shell method with no approximations. These calculations required more than 200 h of computer time on a PDP-12 computer equipped with a floating-point processor.) In the problem of interest in the present work, it will turn out that the problem can be solved exactly and analytically with no approximations.

Model

The macromolecule is modeled as a long cylinder that lies along the z axis with its ends at $z = \pm L/2$. It is assumed that the solvent can be treated as a homogeneous continuum with viscosity η and that it is at rest at distances far from the cylinder. It is further assumed that the only motion of the cylinder involves twisting or torsional motions about its long axis. There are no restrictions placed on how the instantaneous (rotation or torsion) angular velocities vary along the cylinder.

To begin, imagine that a large number of identical, nonoverlapping beads are uniformly placed at a distance a from the z axis to generate a beaded cylinder. The beads are allowed to rotate about the z axis and this rotation rate is allowed to vary for different positions along z. All beads at the same z position are constrained to rotate at the same rate. The velocity perturbation of the solvent at bead l due to the presence of the other beads is given by the well-known equation[13]

$$\mathbf{v}_l' = \mathbf{v}_l - \mathbf{v}_l^0 = \sum_{s \neq l} \mathbf{t}_{ls} \cdot (\mathbf{u}_s - \mathbf{v}_s) \tag{3}$$

where $\mathbf{v}_l'$ is the velocity perturbation of the solvent at bead l, $\mathbf{v}_l$ would be the actual solvent velocity at bead l if bead l were not there, $\mathbf{v}_l^0$ is the solvent velocity at bead l in the absence of all beads, u_s is the actual velocity at bead s, and

$$\mathbf{t}_{ls} = \frac{3b}{4R_{ls}}\left(\mathbf{I} + \frac{\mathbf{R}_{ls}\mathbf{R}_{ls}}{R_{ls}^2}\right) - \frac{b^3}{4R_{ls}^3}\left(\frac{3\mathbf{R}_{ls}\mathbf{R}_{ls}}{R_{ls}^2} - \mathbf{I}\right) \tag{4}$$

where b is the bead radius, R_{ls} is the distance between beads l and s, $\mathbf{I}$ is the unit tensor, and $\mathbf{R}_{ls}\mathbf{R}_{ls}/R_{ls}^2$ is a second rank Cartesian tensor or dyad.

Since the solvent is at rest in the absence of beads, $\mathbf{v}_l^0 = 0$. Furthermore, we can write

$$\begin{aligned}\mathbf{u}_s - \mathbf{v}_s &= [\omega_s(\text{bead}) - \omega_s(\text{solvent})] \times \mathbf{a}_s \\ &= \frac{1}{\gamma_b}\mathbf{T}_s \times \mathbf{a}_s\end{aligned} \tag{5}$$

where ω_s(bead/solvent) is the angular rotation vector at bead/solvent position $\mathbf{s}$, $\mathbf{a}_s$ is a radial position vector at bead s, $\mathbf{T}_s$ is the torque on bead s, and γ_b is the rotational friction coefficient of a single bead of radius b rotating at a distance a from the axis. It is given by[20]

$$\gamma_b = 6\pi\eta b a^2 + 8\pi\eta b^3 \tag{6}$$

Assuming the beads are all small compared to the distance a, the second term in both eq 4 and eq 6 can be ignored and eq 2 can be written

$$\mathbf{v}_l = \sum_{s \neq l} \mathbf{H}_{ls} \cdot [\mathbf{T}_s \times \mathbf{a}_s] \tag{7}$$

where

$$\mathbf{H}_{ls} = \frac{1}{8\pi\eta a^2 R_{ls}}\left(\mathbf{I} + \frac{\mathbf{R}_{ls}\mathbf{R}_{ls}}{R_{ls}^2}\right) \tag{8}$$

Now imagine taking the simultaneous limits of zero bead size and infinite bead number. Replacing the sum in eq 7 with an integral, we can write

$$\mathbf{v}_l = \int{}' \mathrm{d}s\, \mathbf{H}_{ls} \cdot [\mathbf{T}_s \times \mathbf{a}_s] \tag{9}$$

where the prime signifies that the term $s = l$ is excluded. The integral over bead index can be replaced by a surface integral

$$\mathrm{d}s \to \sigma\, \mathrm{d}A = \sigma a\, \mathrm{d}\phi\, \mathrm{d}z \tag{10}$$

where σ denotes the number of beads per unit area, and $\{a, \phi, z\}$ are cylindrical coordinates of some point $\mathbf{R}$ on the cylinder surface. Also, the torque on beads at position $\mathbf{R}$ can be defined in terms of a torque per unit length, $\tau(R)$, by

$$\mathbf{T}_s = \frac{1}{2\pi a \sigma}\tau(\mathbf{R}) \tag{11}$$

If bead l in eq 7 is at point R', then we can write

$$\mathbf{v}(\mathbf{R}') = \frac{1}{2\pi}\int \mathrm{d}\phi\, \mathrm{d}z\, \mathbf{H}(\mathbf{R}' - \mathbf{R}) \cdot [\tau(\mathbf{R}) \times \mathbf{a}(\mathbf{R})] \tag{12}$$

In eq 12, $\mathbf{v}(\mathbf{R}')$ represents the solvent velocity at the position $\mathbf{R}'$ on the cylinder surface in the limit of an infinite number of beads. For stick boundary conditions, $\mathbf{v}(\mathbf{R}')$ is also the instantaneous velocity of the cylinder at the point $\mathbf{R}'$. $\mathbf{v}(\mathbf{R}')$ can be written

$$\mathbf{v}(\mathbf{R}') = \omega(\mathbf{R}') \times \mathbf{a}(\mathbf{R}') \tag{13}$$

and since

$$\mathbf{a}(\mathbf{R}') \times \mathbf{v}(\mathbf{R}') = a^2 \omega(\mathbf{R}') \tag{14}$$

we finally have

$$\omega(\mathbf{R}') = \frac{1}{2\pi a^2}\int_{-L/2}^{+L/2} \mathrm{d}z \int_0^{2\pi} \mathrm{d}\phi\, \mathbf{a}(\mathbf{R}') \times \{\mathbf{H}(\mathbf{R}' - \mathbf{R}) \cdot [\tau(\mathbf{R}) \times \mathbf{a}(\mathbf{R})]\} \tag{15}$$

In the Appendix, it is shown that eq 15 can be written

$$\omega(z') = \frac{1}{16\pi^2 a^2 \eta}\int_{-L/2}^{+L/2} \mathrm{d}z\, \tau(z) \int_0^{2\pi} \mathrm{d}\phi \left[\frac{\cos\phi}{r} + \frac{a^2}{r^3}\sin^2\phi\right] \tag{16}$$

where $r = [(z' - z)^2 + 2a^2(1 - \cos\phi)]^{1/2}$. The quantity in brackets in eq 16 is easiest to solve by using the Green's function expansion of $1/r$ in cylindrial coordinates[21]

$$\frac{1}{r} = \frac{4}{\pi}\int_0^\infty \mathrm{d}k \cos[k(z - z')] \times \left\{\tfrac{1}{2}I_0(ka)K_0(ka) + \sum_{m=1}^{\infty} \cos(m\phi) I_m(ka) K_m(ka)\right\} \tag{17}$$

where I_m and K_m are modified Bessel functions. The quantity $1/r^3$ is readily evaluated by noting

$$\frac{\partial}{\partial\phi}\left(\frac{1}{r}\right) = -\frac{a^2 \sin\phi}{r^3} \tag{18}$$

Hence

$$\frac{1}{r^3} = \frac{1}{a^2 \sin\phi}\left\{\frac{4}{\pi}\int_0^\infty \mathrm{d}k \cos[k(z - z')] \times \sum_{m=1}^{\infty} m \sin(m\phi) I_m(ka) K_m(ka)\right\} \tag{19}$$

Using eq 17 and 19 we have

$$\frac{\cos\phi}{r} + \frac{a^2 \sin^2\phi}{r^3} = \frac{4}{\pi}\int_0^\infty \mathrm{d}k \cos[k(z - z')]\left\{\tfrac{1}{2}I_0(ka)K_0(ka)\cos\phi + \sum_{m=1}^{\infty} [\cos\phi \cos(m\phi) + m \sin\phi \sin(m\phi)] I_m(ka) K_m(ka)\right\} \tag{20}$$

The ϕ integration in eq 16 then gives

$$\int_0^{2\pi} \mathrm{d}\phi \left[\frac{\cos\phi}{r} + \frac{a^2 \sin^2\phi}{r^3} \right] = 8\int_0^\infty \mathrm{d}k \cos\left[k(z - z')\right] I_1(ka) K_1(ka) \quad (21)$$

Combining this result with eq 16, we finally have

$$\omega(z') = \frac{1}{2\pi^2 a^2 \eta} \int_0^\infty \mathrm{d}k\, I_1(ka) K_1(ka) \int_{-L/2}^{+L/2} \mathrm{d}z\, \tau(z) \cos\left[k(z' - z)\right] \quad (22)$$

Equation 22 is a general result and shows how the instantaneous angular velocity at the point z' is related to the hydrodynamic torque per unit length acting on the entire cylinder. Note that in general, it is not possible to define a friction coefficient since it implies a one-to-one correspondence between $\omega(z)$ and $\tau(z)$. The assumptions made in deriving eq 22 are as follows: (1) the solvent can be treated as a homogeneous continuum with viscosity η and is at rest far from the cylinder, (2) the Oseen tensor, eq 3 and 4, correctly accounts for the hydrodynamic interactions if the cylinder surface is modeled by a large number of small, identical beads of uniform surface density, and (3) stick boundary conditions hold.

Application to Torsional Brownian Motions

Equation 22 can be evaluated for a number of special cases. The simplest involves a long cylinder in which the hydrodynamic torque per unit length is assumed constant. This corresponds to a long cylinder undergoing uniform rotation and yields the familiar Perrin formula given by eq 2. The case in which the hydrodynamic torque per unit length varies sinusoidally along the cylinder is simple to solve. Assume

$$\tau(z) = \tau_0 \cos(qz + \epsilon) \quad (23)$$

where τ_0 is the amplitude of the hydrodynamic torque, $2\pi/q$ is the distance along the cylinder for a complete cycle of the torque, and ϵ is a phase factor. For the case of a very long cylinder, eq 22 can be written

$$\omega(z') = \frac{\tau_0}{2\pi^2 a^2 \eta} \times \int_0^\infty \mathrm{d}k\, I_1(ka) K_1(ka) \int_{-\infty}^{+\infty} \mathrm{d}z \cos(qz + \epsilon) \cos(k(z' - z)) \quad (24)$$

provided z' is not near the end of the cylinder. By expressing the cosines in eq 24 in complex exponential form and making use of the following representation of the δ function

$$\delta(q - k) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \mathrm{d}z\, e^{iz(q-k)} \quad (25)$$

it follows that

$$\omega(z') = \frac{\tau(z')}{2\pi a^2 \eta} I_1(qa) K_1(qa) \quad (26)$$

Comparing this result with eq 1, it can be seen that the corresponding friction coefficient can be written

$$\gamma(q) = \frac{2\pi a^2 \eta}{I_1(qa) K_1(qa)} \quad (27)$$

For $qa \ll 1$, corresponding to a variation in torque or angular velocity that is gradual compared to the thickness of the cylinder, eq 27 reduces to the Perrin result as it must. On the other hand, $\gamma(q)$ may deviate substantially from the Perrin result when this condition is not satisfied.

Table I
Friction Coefficients and Approximate Relaxation Times of Several Short Normal Modes of DNA[a]

$2\pi/q$ (base pairs)	$\gamma/\gamma_{\mathrm{bp}}$	approx relax time, ns
2	11.130	0.001
10	2.421	0.104
20	1.538	0.405
30	1.303	0.900
40	1.199	1.61
50	1.142	2.51
80	1.069	6.43
200	1.016	40.2

[a] See text for details.

Equation 27 is important in connection with the dynamical theory of torsion in linear macromolecules.[6,7] On the basis of recent fluoresecence depolarization experiments, it has been concluded that native DNA behaves like a torsionally uniform elastic filament.[3,4] The torsional motion at a particular position and time can be thought of as a linear superposition of normal modes that vary sinusoidally along the helix. The friction coefficient corresponding to a particular normal mode is then given by eq 27.

In the theories of Barkley and Zimm[6] and Allison and Schurr[7] the actual friction was approximated using the Perrin result. In the latter theory, the DNA was modeled by $N + 1$ identical rigid rods, which can be taken here to be 1 base pair in length, linked end-to-end by Hookean torsion springs and undergoing collective torsional Brownian motion about their fixed rod axes. The wavelength of normal mode k, in base pairs, is given by

$$L_k = 2(N + 1)/(k - 1) \quad \text{base pairs} \quad (28)$$

where $1 \leq k \leq N + 1$. The case $k = 1$ corresponds to the uniform mode and $k = N + 1$ corresponds to the shortest mode in which all base pairs twist in opposite directions on going from one base pair to the next. The approximate relaxation time associated with mode k is given by

$$t_k = \gamma_{\mathrm{bp}}/[4\alpha \sin^2(\pi/L_k)] \quad (29)$$

where γ_{bp} is the (approximate) friction coefficient for a base pair of length 3.4 Å and α is the torsional force constant between base pairs.[7]

Table I summarizes some of the results of this section and uses eq 27–29. It was assumed that a = 12 Å in eq 27. In calculating the relaxation times, use was made of the results of Thomas et al.;[3] $\alpha = 1.38 \times 10^{-12}$ dyn cm, $\gamma_{\mathrm{bp}} = 5.47 \times 10^{-23}$ dyn cm s. The main point of Table I is that the normal mode relaxation times calculated using eq 29 (third column) are incorrect since the friction constants are incorrect, at least for normal modes shorter than about 100 base pairs.

From the fluorescence depolarization experiments,[2-4] it can be concluded that most of the depolarization results from the concerted motions of between 80 and 200 base pairs and that this takes place over a time interval between 5 and 40 ns. On this basis, the Perrin formula is probably a good approximation. Nonetheless, Thomas et al.[3] observed a small, but detectable depolarization between 0.2 and 2.5 ns, corresponding to a normal mode length of 50 base pairs and less. It was further concluded that the time resolution of the experiment was such that normal mode lengths of as few as 20 base pairs could be detected. For these rapid modes, the Perrin result underestimates the actual friction significantly and on this basis, it can be

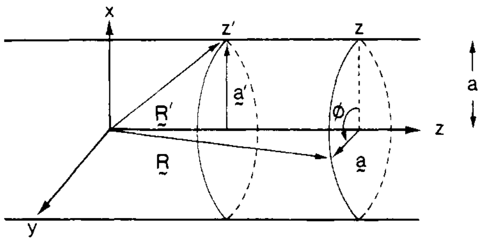

Figure 1. Geometry for the elastic cylinder model. **R**′ and **R** are position vectors, **a**′ and **a** are radial vectors from the axis of rotation, and z' and z denote positions along the axis of rotation. **a**′ is chosen to lie along the x axis ($\phi' = 0$).

concluded that the theory needs to account more accurately for hydrodynamic interaction if it is to be applied at times shorter than several nanoseconds.

It is worthwhile at this point to consider other assumptions of features of the model which may limit analysis at times shorter than several nanoseconds. Some of these pertain to both the dynamical theory of torsion in macromolecules[6,7] and also the extrapolated shell method used to derive eq 22. In both cases, modeling the macromolecule as a homogeneous, torsionally elastic cylinder is valid as long as the wavelength of the normal mode is large compared to local variations in the structure. In the case of DNA, we can expect this to be true for normal modes of wavelength 10 base pairs or more, corresponding to relaxation times in excess of 0.10 ns.

It is also assumed that the macromolecule is surrounded by a liquid continuum characterized by a viscosity η. At sufficiently short times or high frequencies, the solvent exhibits the properties of a solid rather than a liquid.[22] It is not known where this transition occurs in water, but it can be expected to take place at times comparable to the molecular reorientation times. Since the dielectric relaxation time of water is 1×10^{-12} s,[23] it can be anticipated that the transition from solid to liquid-like behavior occurs on the picosecond time scale.

With regards to the shell model, it is assumed that the Oseen tensor properly accounts for the hydrodynamic interaction. From eq 3, it can be seen that the velocity perturbation at some point depends on the state of the system at the same instant. In other words, no retardation effects are included in the Oseen tensor. However, since a mechanical perturbation in the solvent can be expected to propagate at the speed of sound, which is approximately 1.7×10^6 Å/ns, retardation effects on the Oseen tensor should be unimportant.

One last assumption that is rather difficult to deal with is the assumption that stick boundary conditions adequately describe the cylinder–solvent interface. In the case of rotational motion, stick boundary conditions undoubtedly hold for macromolecules with a molecular weight of 10 000 or more,[24] but for small molecules (molecular weight up to 300) it appears that a condition intermediate between stick and slip holds.[24,25] Unfortunately, the molecular weight range between 300 and 10 000 has not been studied in sufficient detail to determine where the stick boundary condition breaks down. To be cautious, we might reasonably expect stick boundary conditions to be valid for a particular normal mode provided its corresponding molecular weight exceeds 10 000. In the case of DNA this corresponds to 15 base pairs or more or relaxation times of 0.23 ns or longer.

Conclusions

On the basis of the previous section, it can be concluded that current dynamical theory of torsion in macromolecules is valid down to 5 ns and that proper inclusion of hydrodynamic interaction would extend its range of validity down to approximately 0.1 ns. Work on just that problem is now well under way in this laboratory and shall be submitted shortly. At still shorter times, such factors as deviations from stick boundary conditions, local structural features, and possibly solvent viscoelasticity become problems.

This has been one application of eq 22 and other useful applications undoubtedly exist. For example, a slowly migrating protein bound to DNA may produce a large, localized torque in the neighborhood to which it is bound.[26] Equation 22 could then be used to study what effect that protein has on local dynamics.

Acknowledgment. The author thanks Professor John Schellman for support. This research was funded in part by grants from the United States Public Health Service (GM 20195) and the National Science Foundation (PCM 8104339) (both to J.A.S.) and by Fellowship No. 1 F32 GM 08090-01 from the National Institutes of Health.

Appendix

The geometry of the problem is shown in Figure 1. Because of the symmetry of the problem, **a**′ can be chosen to lie along the x axis without loss of generality. The various vectors of interest are

$$\mathbf{a}(\mathbf{R}) = a(\cos(\phi\hat{i}) + \sin(\phi\hat{j})) \tag{A1}$$

$$\mathbf{a}(\mathbf{R}') = a\hat{i} \tag{A2}$$

$$\tau(\mathbf{R}) = \tau(z)\hat{k} \tag{A3}$$

where $\hat{i}$, $\hat{j}$, and $\hat{k}$ denote unit vectors along x, y, and z, respectively. The tensor $\mathbf{H}(\mathbf{R}' - \mathbf{R})$ can be written

$$\mathbf{H}(\mathbf{R}'-\mathbf{R}) = \frac{1}{8\pi\eta r a^2} \times \begin{bmatrix} 1 + \frac{a^2}{r^2}(1-\cos\phi)^2 & -\frac{a^2}{r^2}(1-\cos\phi)\sin\phi & \frac{a}{r^2}(z'-z)(1-\cos\phi) \\ -\frac{a^2}{r^2}(1-\cos\phi)\sin\phi & 1+\frac{a^2}{r^2}\sin^2\phi & -\frac{a}{r^2}(z'-z)\sin\phi \\ \frac{a}{r^2}(z'-z)(1-\cos\phi) & -\frac{a}{r^2}(z'-z)\sin\phi & 1+\frac{(z'-z)^2}{r^2} \end{bmatrix} \tag{A4}$$

where

$$r \equiv |\mathbf{R}' - \mathbf{R}| = [(z'-z)^2 + 2a^2(1-\cos\phi)]^{1/2} \tag{A5}$$

It is then straightforward to show that

$$\mathbf{a}(\mathbf{R}') \times \{\mathbf{H}(\mathbf{R}'-\mathbf{R})\cdot[\tau(\mathbf{R}) \times \mathbf{a}(\mathbf{R})]\} = \frac{\tau(z)\hat{k}}{8\pi\eta}\left(\frac{\cos\phi}{r} + \frac{a^2\sin^2\phi}{r^3}\right) \tag{A6}$$

There is actually a $\hat{j}$ component that has been ignored in eq A6 since simple inspection verifies that this term vanishes upon integration over ϕ. Substitution of eq A6 in (21) leads directly to eq 22.

References and Notes

(1) Perrin, F. *J. Phys. Radiat.* **1934**, *5*, 497; **1936**, *7*, 1.
(2) Wahl, Ph.; Paoletti, J.; LePecq, J. B. *Proc. Natl. Acad. Sci. U.S.A.* **1970**, *65*, 417.
(3) Thomas, J. C.; Allison, S. A.; Appellof, C. J.; Schurr, J. M. *Biophys. Chem.* **1980**, *12*, 177.
(4) Millar, D. P.; Robbins, R. J.; Zewail, A. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 5593.
(5) Robinson, B. H.; Forgacs, G.; Dalton, L. R.; Frisch, H. L. *J. Chem. Phys.* **1980**, *73*, 4688.

(6) Barkley, M. S.; Zimm, B. H. *J. Chem. Phys.* **1979**, *70*, 2991.
(7) Allison, S. A.; Schurr, J. M. *Chem. Phys.* **1979**, *41*, 35.
(8) Allison, S. A.; Shibata, J. H.; Wilcoxon, J.; Schurr, J. M. *Biopolymers*, **1982**, *21*, 729.
(9) Carpenter, D. K.; Skolnick, J. *Macromolecules* **1981**, *14*, 1284.
(10) Swanson, E.; Teller, D. C.; de Haën, C. *J. Chem. Phys.* **1978**, *68*, 5097.
(11) Teller, D. C.; Swanson, E.; de Haën, C. *Methods Enzymol.* **1979**, *61*, 103.
(12) Bloomfield, V.; Dalton, W. O.; Van Holde, K. E. *Biopolymers* **1967**, *5*, 135.
(13) Oseen, C. W. "Mathematik and ihre Anwenudungen in Monographien and Lehrbüchern"; Hilb, E., Ed.; Akademische Verlagsgresellschaft: Leipzig, 1927; Vol. 1.
(14) Rotne, J.; Prager, S. *J. Chem. Phys.* **1969**, *50*, 4831.
(15) Yamakawa, H. *J. Chem. Phys.* **1970**, *53*, 436.
(16) Garcia de la Torre, J.; Bloomfield, V. *Biopolymers* **1977**, *16*, 1747, 1765.
(17) Garcia de la Torre, J.; Bloomfield, V. *Q. Rev. Biophys.* **1981**, *14*, 81.
(18) Kirkwood, J. G. *J. Polym. Sci.* **1954**, *12*, 1.
(19) Allison, S. A.; Easterly, R. A.; Teller, D. C. *Biopolymers* **1980**, *19*, 1475.
(20) Happel, J.; Brenner, H. "Low Reynolds Number Hydrodynamics"; Leyden: Noordhoff, 1973.
(21) Jackson, J. D. "Classical Electrodynamics"; Wiley-Interscience: New York, 1975.
(22) Landau, L. D.; Lifschitz, E. M. "Theory of Elasticity"; Pergamon Press: New York, 1959; Vol. 7.
(23) Collie, C. H.; Hasted, J. B.; Riston, D. M. *Proc. Phys. Soc. London* **1948**, *60*, 145.
(24) Berne, B.; Pecora, R. "Dynamic Light Scattering"; Wiley-Interscience: New York, 1976.
(25) Bauer, D. R.; Brauman, J. I.; Pecora, R. *J. Am. Chem. Soc.* **1974**, *96*, 6840.
(26) Schurr, J. M. *Biophys. Chem.* **1979**, *9*, 413.

Generalized View of Molecular Weight Dependence of Microdomain Size of Block Polymers. Appraisal of Hadziioannou–Skoulios' Data on Binary Mixtures of Block Polymers

Takeji Hashimoto

Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan. *Received January 29, 1982*

ABSTRACT: An appraisal of Hadziioannou–Skoulios' data on binary mixtures of block polymers α and β has been carried out to derive a scaling rule relating microdomain size with average molecular weight of the mixture. The mixtures as well as the pure block polymers α and β studied in this work have the lamellar microdomain. Hadziioannou–Skoulios' results on the lamellar identity period D of the mixtures are found to be summarized as $D \sim \bar{M}_n{}^a$ and $S/N \sim \bar{M}_n{}^{1-a}$, where $a = {}^2/_3$ to ${}^4/_5$ for the molecular weight range covered in this study, $\bar{M}_n$ is the number-average molecular weight of the block polymers in the mixture, and S/N is the average interfacial area occupied per chemical junction point of the block polymers. This result is a generalized form obtained for the pure block polymer, for which $\bar{M}_n$ should be replaced by the molecular weight of the block polymer.

I. Introduction

We discuss here the relationship between the size of the microdomain structure of amorphous block polymers and the molecular weight of the block polymer composed of A and B polymer chains under a strong segregation limit where A and B exert a strong repulsive potential; i.e., $\chi_{AB}Z \gg 2$ (χ_{AB} being the Flory–Huggins interaction parameter between A and B and Z being the total degree of polymerization for the block chain).[1,2] For pure block polymers having a very narrow molecular weight distribution, this relationship has been extensively studied, and the following scaling rule has been derived for polystyrene–polyisoprene (SI) and polystyrene–polybutadiene (SB) di- and triblock polymers giving rise to the lamellar microdomains[3] over the range of molecular weights M_t from ca. 2×10^4 to 2×10^5:

$$D_l = 0.024 M_t^{2/3}\ (\text{nm}) \tag{1}$$

$$(S/N)_l = 0.14 M_t^{1/3}\ (\text{nm}^2) \tag{2}$$

where D_l is the identity period of the lamellar microdomains, $(S/N)_l$ is the average interfacial area occupied by a single chemical junction point of the block polymer, and M_t is the total molecular weight. It should be noted that for ABA triblock polymers, M_t refers to the molecular weight of the diblock polymers A–(1/2)B. It has also been shown[3] that this rule, obtained for a limited range of molecular weight, can be quantitatively explained in terms of equilibrium theories based upon statistical mechanical treatments of random flight chains in confined space.[4-8] However, it should be noted that the theories indicate that the functional form $D \sim M^a$ is not very good over the whole molecular weight range and a is not exactly equal to ${}^2/_3$ even in the high molecular weight limit. Since this point is essential, we will clarify it more rigorously below in the context of Helfand–Wasserman's *narrow interphase approximation.*[7]

The free energy density of the microdomain formation f is given by[7]

$$f(D_l) = c_1(M_t/D_l) + c_2(D_l/M_t^{1/2})^p + c_3 \log D_l \tag{3}$$

where the coefficient c_i's are constants independent of molecular weight M_l and identity period D_l but dependent on Kuhn's statistical segment length, densities, the interaction parameter χ, etc. The first term on the right-hand side of eq 3 arises from surface free energy, the second term from the constraint entropy loss (loss of entropy from confining the chains in their respective domains), and the third term from the placement entropy loss (loss of entropy from confining the chemical junction points in the interfacial regions). The constant p was numerically evaluated to be 2.5.[7] In the high molecular

0024-9297/82/2215-1548$01.25/0