(43) D. R. Reid, *Br. Plast.*, 2 (1959).
(44) D. J. Plazek, E. Riande, H. Markovitz, and N. Raghupathi, *J. Polym. Sci., Polym. Phys. Ed.*, 17, 2189 (1979).
(45) D. J. Plazek, *J. Colloid Sci.*, 15, 50 (1960).
(46) D. J. Plazek, V. Tan, and V. M. O'Rourke, *Rheol. Acta*, 13, 367 (1974).
(47) N. Raghupathi, Ph.D. Thesis, University of Pittsburgh, 1975.
(48) S. J. Orbon and D. J. Plazek, *J. Polym. Sci., Polym. Phys. Ed.*, 17, 1871 (1979).
(49) W. W. Graessley and S. F. Edwards, *Polymer*, 22, 1329 (1981).
(50) M. Kurata and W. H. Stockmayer, *Adv. Polym. Sci.*, 3, 197 (1963).
(51) J. B. Kinsinger and R. E. Hughes, *J. Phys. Chem.*, 67, 1922 (1963).

Screening of Hydrodynamic Interaction in a Solution of Rodlike Macromolecules

M. Muthukumar*

Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616

S. F. Edwards

Cavendish Laboratory, University of Cambridge, Cambridge, England CB3 0HE.
Received February 1, 1983

ABSTRACT: Using an effective medium argument, we show that the screening of hydrodynamic interactions has only a weak effect on the zero-shear-rate viscosity of a solution of rodlike molecules. The hydrodynamic screening length (ξ) varies with the monomer density (ρ) as $\xi \approx \rho^{-1/2}$, in contrast with $\xi \sim \rho^{-1}$ for the case of a solution of flexible chains under similar conditions.

Introduction

It is well-known[1] that for a dilute solution of long rodlike macromolecules the intrinsic viscosity ($[\eta]$) is proportional to M^2 if the hydrodynamic interaction is completely ignored (where M is the molecular weight of the rod). The incorporation[1-6] of hydrodynamic interactions leads to the familiar result $[\eta] \sim M^2/\ln M$. When the number density of the rods in the solution is increased, the hydrodynamic interaction between any two space points in the fluid is progressively screened. The concentration dependence of the screening is derived in this paper. We show that the specific viscosity, $(\eta - \eta_0)/\eta_0\rho$, is proportional to $M^2/\ln \rho$ in the high-concentration limit, where ρ is the monomer density and η and η_0 are the viscosities of the solution and solvent, respectively.

The analogous results for solutions of flexible chains are the following.[7,8] When hydrodynamic interaction is ignored, $[\eta] \propto M$. The incorporation of the hydrodynamic interaction leads to $[\eta] \propto M^{1/2}$. In the dense limit, where the hydrodynamic interaction is completely screened, $[(\eta - \eta_0)/\eta_0\rho] \propto \rho M$. Thus the hydrodynamic interaction plays a less pronounced role in the transport properties of solution of slender rods than in the case of flexible chains.

In the treatment of the transport coefficients of solutions of rods, it is necessary to introduce a cutoff at short distances.[1-6] However, it does not matter what this cutoff is since a proper solution is not yet available in this limit anyway. For simplicity, we consider the Riseman–Kirkwood–Auer model[3,4] for the rod which treats the rod as a line of $2n + 1$ beads separated by a step length l so that the length of the rod is $L = 2nl$. The length of the rod is taken to be very large compared to the diameter (d) of these beads, so that the beads can be treated to be point frictional sources. As mentioned above, any theoretical treatment requires a cutoff at short distances along the rod. We choose the step length l to be this cutoff.

We have deliberately ignored the entanglement effect[9-11] between the various rods, as we are interested here in finding how weak the effect of hydrodynamic interaction is on the transport properties of solutions of rods and what the concentration dependence of the hydrodynamic screening length is. Since the rods begin to get entangled for $c > L^{-3}$ (c = number density of rods), the formulas derived below are valid for L such that $d \ll L \ll c^{-1/3}$. Thus it may be possible to get to the screened regime for a solution of short but thin rods. Although there has been an earlier attempt[12] at describing the hydrodynamic interaction in an entangled semidilute solution of rods, the problem addressed here is even simplier but basic.

The important results derived in this paper are summarized as follows:

(i) The reduced viscosity is given by

$$(\eta - \eta_0)/\eta_0 = (\pi/12)cL^3/\ln (L/l) \qquad \text{low } c$$

$$(\eta - \eta_0)/\eta_0 = (\pi/12)cL^3/E_1(l\xi^{-1}) \qquad \text{high } c \qquad (1)$$

where E_1 is the exponential integral.[13]

(ii) The screening length ξ appearing in eq 1 is given by

$$\xi^{-2}E_1(l\xi^{-1}) = 3\pi cL \qquad (2)$$

Basic Equations

The fluid in the absence of the suspended rods is taken to obey the linearized Navier–Stokes equation (in the steady-state limit).

$$-\eta_0\nabla^2\mathbf{v}(\mathbf{r}) + \nabla p(\mathbf{r}) = \mathbf{F}_e(\mathbf{r}) \qquad (3)$$

Here $\mathbf{v}(\mathbf{r})$ is the velocity field at any space point $\mathbf{r}$, p is the pressure, η_0 is the shear viscosity of the solvent, and $\mathbf{F}_e(\mathbf{r})$ is the external field driving the fluid flow. Assuming that the fluid is incompressible, this equation can be written as an integral equation in terms of the familiar Oseen tensor $\mathbf{G}_0$.

$$\mathbf{v}(\mathbf{r}) = \int d\mathbf{r}'\, \mathbf{G}_0(\mathbf{r} - \mathbf{r}')\cdot\mathbf{F}_e(\mathbf{r}')$$

$$\mathbf{G}_0(\mathbf{R}) = (1/8\pi\eta_0|\mathbf{R}|)(1 + \mathbf{RR}/|\mathbf{R}|^2) \qquad (4)$$

The long-ranged hydrodynamic interaction present in a solvent as given by the Oseen tensor is altered by the presence of rods, and this modification is the origin of the screening of the hydrodynamic interaction. The extent of the screening as a function of the polymer density is derived below.

0024-9297/83/2216-1475$01.50/0

Consider a solution containing N rods each of length L. We adopt the Riseman–Kirkwood model[3] for the rod by taking each rod to contain $2n + 1$ beads with step length l, so that $L = 2nl$. Let $\mathbf{R}_{\alpha i}$ denote the position of the ith bead of αth rod. We assume that the various beads are taken to be point sources of friction, so that the rod is a thin line of length L. Thus we ignore the contribution of the finite diameter (d) of the rod. In the limit of $L \gg d$, the effect of the finite thickness of the rod on the viscosity of the solution is not appreciable as in the case of polymer solutions. We further assume that the dynamics of the rods and the solvent are coupled by the Stokes boundary condition

$$\frac{\partial}{\partial t}\mathbf{R}_{\alpha i} = \mathbf{v}[\mathbf{R}_{\alpha i}] \tag{5}$$

The coupled equations of motion for the combined rods–solvent system can readily be obtained by constructing the Rayleighian of the system, since frictional forces are present. Since this method is outlined elsewhere,[14] we merely give the final equations for the combined system.

$$-\eta_0\nabla^2\mathbf{v}(\mathbf{r}) + \nabla p(\mathbf{r}) = \mathbf{F}_e(\mathbf{r}) + \sum_{\alpha=1}^{N}\sum_{i=1}^{2n+1}\delta(\mathbf{r} - \mathbf{R}_{\alpha i})\sigma_{\alpha i} \quad \sum_{i=1}^{2n+1}\sigma_{\alpha i} = \mathbf{f}_\alpha \tag{6}$$

where $\sigma_{\alpha i}$ is the Lagrange multiplier due to the constraint of eq 5 and can be interpreted as the force density exerted by the ith bead of αth rod into the fluid. The second equation of (6) is the equation of motion for the αth rod, where $\mathbf{f}_\alpha$ is the net random force and the potential forces acting on α.

We now follow the lines of the Freed–Edwards theory[7] for flexible chains to obtain the average velocity field $\mathbf{u}$ at $\mathbf{r}$ in the solution, where $\mathbf{u}(\mathbf{r}) = \langle\mathbf{v}(\mathbf{r})\rangle$, with the angular brackets representing the averages over the centers of mass of all the rods and over all possible orientations of the rods. In this paper, we consider only the isotropic phase, where all orientations of any rod are equally accessible. By performing the above-mentioned average on the first identity of eq 6, we get

$$-\eta_0\nabla^2\mathbf{u}(\mathbf{r}) + \nabla p(\mathbf{r}) - \int d\mathbf{r}'\ \boldsymbol{\Sigma}(\mathbf{r} - \mathbf{r}')\cdot\mathbf{u}(\mathbf{r}') = \mathbf{F}_e(\mathbf{r}) \tag{7}$$

where the last term on the left-hand side contains all the contribution of the rods and is actually the average divergence of the stress tensor arising from rods. By Fourier transforming eq 7 with respect to $\mathbf{r}$ ($\mathbf{k} \sim$ conjugate variable) and defining $-\Sigma(\mathbf{k})/\eta_0 \equiv \xi^{-2}(k)$, we obtain

$$\eta_0[k^2 + \xi^{-2}(k)]\mathbf{u}(\mathbf{k}) + i\mathbf{k}p(\mathbf{k}) = \mathbf{F}_e(\mathbf{k}) \tag{8}$$

Since the Navier–Stokes fluid flow is present even for the whole solution, $\xi^{-2}(k = 0)$ must vanish. It is shown below that this is indeed so. Furthermore, $\xi^{-2}(k)$ varies as k^2 for low k. It is obvious from the structure of eq 8 that the k^2 coefficient of $\xi^{-2}(k)$ yields the change in the shear viscosity due to the presence of rods

$$(\eta - \eta_0)/\eta_0 = \lim_{k\to 0} k^{-2}\xi^{-2}(k) \tag{9}$$

Also, if $\xi^{-2}(k)$ is independent of k, for certain ranges of k, then for these ranges of k the hydrodynamic interaction is screened as

$$\mathbf{u}(\mathbf{r}) = \int d\mathbf{r}'\ \mathbf{G}(\mathbf{r} - \mathbf{r}')\cdot\mathbf{F}_e(\mathbf{r}')$$

$$\mathbf{G}(\mathbf{r}) = \int \frac{d^3k}{(2\pi)^3}\ \frac{\exp(i\mathbf{k}\cdot\mathbf{r})(1 - k^{-2}\mathbf{kk})}{\eta_0(k^2 + \xi^{-2})} \sim \frac{\exp(-|\mathbf{r}|/\xi)}{8\pi\eta_0|r|} \tag{10}$$

Thus when $\xi^{-2}(k)$ becomes independent of k, ξ is the screening length for the hydrodynamic interaction.[8] Therefore, the viscosity of the solution and the extent and the conditions of the screening of hydrodynamic interaction are contained in $\xi^{-2}(k)$, which we now proceed to derive.

Instead of giving a rigorous multiple-scattering analysis, we present here the effective meedium argument.[8] Consider a single chain present in an effective medium whose propagator $\mathbf{g}[\xi(k)]$ is given by eq 10, where $\xi(k)$ is unknown and to be determined. The contribution of one such chain in the effective medium (in terms of unknown $\xi(k)$) to the divergence of the stress tensor when multiplied by N must be equal to $\eta_0\int\xi^{-2}(\mathbf{r} - \mathbf{r}')\cdot\mathbf{u}(\mathbf{r}')\ d\mathbf{r}'$. Then the requirement of self-consistency in $\xi(k)$ leads to the desired expression for $\xi^{-2}(k)$. Thus the derivation is as follows.

For a single chain present in the effective medium described by $\mathbf{g}$ of eq 10, the average velocity field is given by

$$\mathbf{u}'(\mathbf{r}) = \int d\mathbf{r}'\ \mathbf{G}(\mathbf{r} - \mathbf{r}')\cdot\mathbf{F}_e(\mathbf{r}') + \sum_{i=1}^{2n+1}\mathbf{G}(\mathbf{r} - \mathbf{R}_{\alpha i})\cdot\sigma_{\alpha i} \tag{11}$$

Using the boundary condition of eq 5, we obtain

$$\dot{\mathbf{R}}_{\alpha i} = \int d\mathbf{r}'\ \mathbf{G}(\mathbf{R}_{\alpha i} - \mathbf{r}')\cdot\mathbf{F}_e(\mathbf{r}') + \sum_{j=1}^{2n+1}\mathbf{G}(\mathbf{R}_{\alpha i} - \mathbf{R}_{\alpha j})\cdot\sigma_{\alpha j} \tag{12}$$

Define an inverse operator G^{-1} according to

$$\sum_{p=1}^{2n+1}\mathbf{G}^{-1}(\mathbf{R}_{\alpha i},\mathbf{R}_{\alpha p})\cdot\mathbf{G}(\mathbf{R}_{\alpha p} - \mathbf{R}_{\alpha j}) = \mathbf{1}\delta_{ij} \tag{13}$$

where δ_{ij} is the Kronecker delta. Use of eq 13 in eq 12 gives

$$\sigma_{\alpha i} = \sum_{j=1}^{2n+1}\mathbf{G}^{-1}(\mathbf{R}_{\alpha i},\mathbf{R}_{\alpha j})\cdot\left[\dot{\mathbf{R}}_{\alpha j} - \int d\mathbf{r}'\ \mathbf{G}(\mathbf{R}_{\alpha i} - \mathbf{r}')\cdot\mathbf{F}_e(\mathbf{r}')\right] \tag{14}$$

Substitution of eq 14 in the static limit into eq 11 yields

$$\mathbf{u}'(\mathbf{r}) = \mathbf{u}(\mathbf{r}) - \int d\mathbf{r}'\ d\mathbf{r}''\ \mathbf{G}(\mathbf{r} - \mathbf{r}')\cdot \langle\sum_{i,j=1}^{2n+1}\delta(\mathbf{r}' - \mathbf{R}_{\alpha i})\mathbf{G}^{-1}(\mathbf{R}_{\alpha i},\mathbf{R}_{\alpha j})\delta(\mathbf{R}_{\alpha j} - \mathbf{r}'')\rangle\cdot\mathbf{u}(\mathbf{r}'') \tag{15}$$

Thus the contribution of one chain in the effective medium to $\int d\mathbf{r}'\ \boldsymbol{\Sigma}(\mathbf{r} - \mathbf{r}')\cdot\mathbf{u}(\mathbf{r}')$ is

$$\frac{1}{V}\int d\mathbf{r}'\ \langle\sum_{i,j=1}^{2n+1}\delta(\mathbf{r} - \mathbf{R}_{\alpha i})\mathbf{G}^{-1}(\mathbf{R}_{\alpha i},\mathbf{R}_{\alpha j})\delta(\mathbf{R}_{\alpha j} - \mathbf{r}')\rangle\cdot\mathbf{u}(\mathbf{r}') \tag{16}$$

Thus the self-consistency requirement for $\boldsymbol{\xi}^{-2}(\mathbf{r} - \mathbf{r}')$ leads to

$$\boldsymbol{\xi}^{-2}(\mathbf{r} - \mathbf{r}') = \frac{N}{\eta_0 V}\langle\sum_{i,j=1}^{2n+1}\delta(\mathbf{r} - \mathbf{R}_{\alpha i})\mathbf{G}^{-1}(\mathbf{R}_{\alpha i},\mathbf{R}_{\alpha j})\delta(\mathbf{R}_{\alpha j} - \mathbf{r}')\rangle \tag{17}$$

In eq 16 and 17, the angular brackets denote the average over all possible orientations of the rod α, whereas in eq 15, they denote the averaging over the center of mass of α also. Note that G^{-1} in eq 17 depends on ξ^{-2} through eq 13 and 10. By Fourier transforming eq 17, we get

$$\boldsymbol{\xi}^{-2}(k) = \frac{N}{\eta_0 V}\langle\sum_{i,j=1}^{2n+1}\exp[-i\mathbf{k}\cdot(\mathbf{R}_i - \mathbf{R}_j)]\mathbf{G}^{-1}(\mathbf{R}_i - \mathbf{R}_j)\rangle = \frac{N}{\eta_0 V}\sum_{i,j}\langle\exp[-i\mathbf{k}\cdot(\mathbf{R}_i - \mathbf{R}_j)]\rangle\langle\mathbf{G}^{-1}(\mathbf{R}_i - \mathbf{R}_j)\rangle \tag{18}$$

The error introduced by the preaveraging approximation in eq 18 is not known, although the same approximation, in the case of a solution of flexible chains, leads to an error of about 10% in the numerical prefactor. Since our main focus here is on the functional dependence of the screening length on concentration but not on the precision of the numerical prefactor, the preaveraging approximation should be sufficient in the following sections. $\langle G^{-1}\rangle$ and $\xi^{-2}(\mathbf{k})$ are evaluated in the following section.

Calculations

Converting the summations in eq 18 to integrals with the changes of variables $x = i/n$ and $y = j/n$, we obtain

$$\xi^{-2}(k) = \frac{Nn^2}{\eta_0 V}\int_{-1}^{1}\mathrm{d}x\int_{-1}^{1}\mathrm{d}y\ \langle \exp[-i\mathbf{k}\cdot\hat{\mathbf{r}}nl|x-y|]\rangle\langle G^{-1}(x,y)\rangle \quad (19)$$

where $\hat{\mathbf{r}}$ is the unit vector along the direction of the rod. By performing the average over all possible orientations of the rod, we get

$$\langle \exp(-i\mathbf{k}\cdot\hat{\mathbf{r}}nl|x-y|)\rangle = j_0(kln|x-y|) \quad (20)$$

where j_0 is the modified Bessel function of first kind.[13] Expanding $\langle G^{-1}(x,y)\rangle$ in double Fourier series

$$\langle G^{-1}(x,y)\rangle = \sum_{\mu,\mu'=-\infty}^{\infty}\langle G_{\mu\mu'}^{-1}\rangle \exp(i\pi\mu x - i\pi\mu' y) \quad (21)$$

with

$$\langle G_{\mu\mu'}^{-1}\rangle = \tfrac{1}{4}\int_{-1}^{1}\mathrm{d}x\int_{-1}^{1}\mathrm{d}y\ \langle G^{-1}(x,y)\rangle \exp(-\lambda\pi\mu x + i\pi\mu' y)$$

we get from eq 19 and 20

$$\xi^{-2}(k) = \frac{Nn^2}{\eta_0 V}\sum_{\mu=-\infty}^{\infty}\int_{-1}^{1}\mathrm{d}x\int_{-1}^{1}\mathrm{d}y\ j_0(knl|x-y|)\times \langle G_{\mu\mu}^{-1}\rangle \exp[i\pi\mu(x-y)] \quad (22)$$

where only the diagonal terms of $\langle G_{\mu\mu'}^{-1}\rangle$ are kept. This is along the spirit of the Riseman–Kirkwood approximation and is correct asymptotically for large μ values. Using the preaveraging approximation in eq 13, we get

$$G_{\mu\mu}^{-1} = 1/(2n)^2 G_{\mu\mu} \quad (23)$$

where

$$G_{\mu\mu} = \tfrac{1}{4}\int_{-1}^{1}\mathrm{d}x\int_{-1}^{1}\mathrm{d}y\ \langle G(x,y)\rangle \exp[-i\pi\mu(x-y)] \quad (24)$$

Substituting eq 10 for G (after taking an angular average over the tensorial part) into eq 24, we obtain

$$G_{\mu\mu} = \frac{1}{12\pi^2\eta_0}\int_{-1}^{1}\mathrm{d}x\int_{-1}^{1}\mathrm{d}y\int_0^{\infty}\mathrm{d}k\ \frac{k^2 j_0(knl|x-y|)}{k^2+\xi^{-2}(k)}\times \exp[-i\pi\mu(x-y)] \quad (25)$$

where eq 20 has been utilized. Combining eq 22, 23, and 25, we get the desired expression for $\xi^{-2}(k)$ as

$$\xi^{-2}(k) = \frac{6\pi^2 N}{V}\sum_{\mu=1}^{\infty}\int_{-1}^{1}\mathrm{d}x\int_{-1}^{1}\mathrm{d}y\ \frac{j_0(knl|x-y|)\exp[i\pi\mu(x-y)]}{\int_{-1}^{1}\mathrm{d}x'\int_{-1}^{1}\mathrm{d}y'\int_0^{\infty}\mathrm{d}z\ \frac{z^2 j_0(znl|x'-y'|)\exp[-i\pi\mu(x'-y')]}{z^2+\xi^{-2}(z)}} \quad (26)$$

From eq 9 and 26, the viscosity (η) of the solution follows as

$$\frac{\eta-\eta_0}{\eta_0} = -\frac{\rho n l^2}{24\eta_0}\sum_{\mu=1}^{\infty}\int_{-1}^{1}\mathrm{d}x\int_{-1}^{1}\mathrm{d}y\ \frac{|x-y|^2\exp[i\pi\mu(x-y)]}{G_{\mu\mu}} \quad (27)$$

where $G_{\mu\mu}$ is given by eq 25 and 26 and ρ is the monomer density. We now calculate the viscosity of the solution at low and high rod concentrations.

A. Infinite Dilution. Since $\xi^{-2}(k)$ has a leading dependence on ρ to the first power, the ξ^{-2} term in the integral for $G_{\mu\mu}$ in eq 25 can be ignored for very dilute solutions. It then follows that

$$G_{\mu\mu} = \frac{1}{12\pi^2\eta_0}\int_{-1}^{1}\mathrm{d}x\int_{-1}^{1}\mathrm{d}y\int_0^{\infty}\mathrm{d}z\ j_0(znl|x-y|)\times \exp[-i\pi\mu(x-y)] = \frac{1}{24\pi nl\eta_0}\int_{-1}^{1}\mathrm{d}x\int_{-1}^{1}\mathrm{d}y\ \frac{\exp[-i\pi\mu(x-y)]}{|x-y|} \quad (28)$$

Writing the integral on the right-hand side as a summation by going back to the original discretized model for the rod in terms of beads, we get

$$G_{\mu\mu} = \frac{1}{24\pi\eta_0 l n^2}\sum_{i,j=-n}^{n}|i-j|^{-1}\exp(-i\pi\mu|i-j|/n) = \frac{1}{6\pi\eta_0 ln}\int_1^{\infty}\frac{\mathrm{d}x}{x}\cos(\pi\mu x/n) = -\frac{\mathrm{Ci}(\pi\mu/n)}{6\pi\eta_0 ln} \quad (29)$$

where Ci is the cosine integral.[13]

Substitution of eq 29 into eq 27 gives

$$\frac{\eta-\eta_0}{\eta_0} = \frac{NL^3}{2\pi V}\sum_{\mu=1}^{\infty}1/\mu^2[-\mathrm{Ci}(\pi\mu/n)] \quad (30)$$

This is the same result as of Riseman–Kirkwood–Auer in the non-free-draining limit as it must be, but the numerical prefactor cannot be taken seriously due to the introduction of cutoff at short distances and omission of rotary degree of freedom. In the limit of very large n, Ci (x) is ln (γx), where $\gamma = 1.781$. Ignoring the μ dependence of Ci, the intrinsic viscosity $[\eta]$ of the solution follows from eq 30 as

$$\frac{\eta-\eta_0}{\eta_0} = \frac{\pi\rho l L^2}{12\ln(L/l)}$$

$$[\eta] = \pi N_A L^3/12M\ln(L/l) \quad (31)$$

where N_A is the Avogadro number and M is the molecular weight.

The adoption of a different model for the rod (for example, an explicit consideration of the rotational motion of the rod) is expected to give a different numerical prefactor for $[\eta]$. However, the essential behavior of $\rho M^2/\ln M$ for $[\eta]$ is valid for sufficiently large molecular weights.

B. Screening Length. For the small-k limit, $\xi^{-2}(k)$ given by eq 26 is proportional to k^2, satisfying the Navier–Stokes fluid flow symmetry. Thus, there is no hydrodynamic screening for large characteristic length scales comparable to the size of the container. However, for large k such that $1/l > k > 1/L$, ξ^{-2} becomes independent of k provided the denominator of the integrand of eq 26 is independent of μ. If this is true, then there is hydrodynamic screening. Assuming for now that the denominator of eq 26 is independent of μ, we obtain

$$\xi^{-2}(k) \sim \frac{6\pi^2 N}{V}\sum_{\mu=1}^{\infty}\int_{-1}^{1}\mathrm{d}x\int_{-1}^{1}\mathrm{d}y\ j_0(knl|x-y|)\exp[i\pi\mu(x-y)] = \frac{12\pi^2 N}{Vnl}\sum_{\mu=1}^{\infty}\int_{-\infty}^{\infty}\mathrm{d}s\ j_0(k|s|)\exp(iq's) = \frac{12\pi^2 N}{Vk}\int_{\pi/nl}^{\infty}\mathrm{d}q'\,\theta(1-q'/k) = \frac{12\pi^2 N}{V}(1-\pi/knl) \simeq 12\pi^2 N/V \quad (32)$$

where $q' = \pi\mu/nl$ and $\theta(x)$ is the step function. Thus $\xi^{-2}(k)$ is independent of k under the above-mentioned condition. Now we look for the self-consistent condition that makes the denominator of eq 26 independent of μ. Let ρ be very large. Since $\xi^{-2}(z)$ is proportional to ρ as the leading power, the z intergral in eq 26 is dominated by large z values. For such large z values, the oscillations due to $\exp[-i\pi\mu(x-y)]$ are overwhelmed by those of j_0. Therefore, this term turns out to be

$$\int_{-1}^{1}\mathrm{d}x\int_{-1}^{1}\mathrm{d}y\int_{0}^{\infty}\mathrm{d}z\ \frac{z^2}{(z^2+\xi^{-2})}j_0(znl|x-y|) = \frac{\pi}{L}\int_{-1}^{1}\mathrm{d}x\int_{-1}^{1}\mathrm{d}y\ |x-y|^{-1}\exp(-nl|x-y|/\xi) = \frac{\pi}{nL}\sum_{i,j=-n}^{n}|i-j|^{-1}\exp(-l|i-j|/\xi) = \frac{4\pi}{L}\int_{l}^{nl}\frac{\mathrm{d}s}{s}\exp(-s/\xi) = \frac{4\pi}{L}E_1(l/\xi) \quad (33)$$

where E_1 is the exponential integral.[13] In obtaining the last equality, nl is taken to be ∞. Use of eq 32 and 33 in eq 26 gives

$$\xi^{-2} = 3\pi\rho l/E_1(l/\xi) \quad (34)$$

This equation gives the hydrodynamic screening length in terms of monomer density ρ.

C. Screened Limit. When the hydrodynamic interaction is screened, the viscosity of the solution is obtained from eq 9, 26, and 33 as

$$\frac{\eta-\eta_0}{\eta_0} = -\frac{3\pi NLn^2l^2}{12VE_1(l/\xi)}\sum_{\mu=1}^{\infty}\int_{-1}^{1}\mathrm{d}x\int_{-1}^{1}\mathrm{d}y\ |x-y|^2\exp[i\pi\mu(x-y)] = \pi NL^3/12VE_1(l/\xi) = \pi\rho lL^2/12E_1(l/\xi) \quad (35)$$

where ξ is given by eq 34. Thus the only change in the viscosity due to the screening of hydrodynamic interaction is the replacement of ln M by ln ρ in the denominator.

Conclusions

By considering an isotropic solution of thin rods such that $d \ll L < c^{-1/3}$ (where d, L, and c are the diameter, total length, and the number density of the rods, respectively), the concentration dependence of the hydrodynamic screening length is derived. The relative viscosity changes from $\rho M^2/\ln M$ for very dilute solutions to $\rho M^2/\ln(l/\xi)$ for high concentrations, where ρ is the monomer density. The screening length is given by eq 34. Since the exponential integral is in general a weak function, ξ varies approximately as $\rho^{-1/2}$. Furthermore, the screening of the hydrodynamic interaction does not appreciably increase the viscosity for this problem.

These results are to be contrasted with those of a solution of flexible chains, where the screening of the hydrodynamic interaction increases the viscosity by a factor of $\rho M^{1/2}$ and ξ varies as ρ^{-1} under similar conditions.

As we are interested here only in the nature of the hydrodynamic screening, we have treated the simplest model for the rod. The better models dealt with in the literature for the single-rod problem can readily be discussed for the concentration-dependent viscosity of the solution. However, these models would alter only the numerical factors but not the functional nature.

In our treatment we have completely ignored the entanglement effects and it is not clear how ξ is affected by the entanglement constraints.

Acknowledgment is made to the National Science Foundation (Grant No. DMR-8112968) and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

References and Notes

(1) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.
(2) Simha, R. *J. Phys. Chem.* **1940**, *44*, 22.
(3) Riseman, J.; Kirkwood, J. G. *J. Chem. Phys.* **1950**, *18*, 512.
(4) Kirkwood, J. G.; Auer, P. L. *J. Chem. Phys.* **1951**, *19*, 281.
(5) Ullman, R. *J. Chem. Phys.* **1964**, *40*, 2422.
(6) Kirkwood, J. G.; Plock, R. J. *J. Chem. Phys.* **1956**, *24*, 665.
(7) Freed, K. F.; Edwards, S. F. *J. Chem. Phys.* **1974**, *61*, 3626.
(8) Muthukumar, M.; Edwards, S. F. *Polymer* **1982**, *23*, 345.
(9) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 560, 918.
(10) Jain, S.; Cohen, C. *Macromolecules* **1981**, *14*, 759.
(11) Frenkel, D.; Maguire, J. F. *Phys. Rev. Lett.* **1981**, *47*, 1025.
(12) Fesciyan, S.; Dahler, J. S. *Macromolecules* **1982**, *15*, 517.
(13) Abramowitz, M.; Stegun, I. A. "Handbook of Mathematical Functions"; Dover: New York, 1972.
(14) Muthukumar, M. *J. Phys. A: Math. Gen.* **1981**, *14*, 2129.