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July 1987

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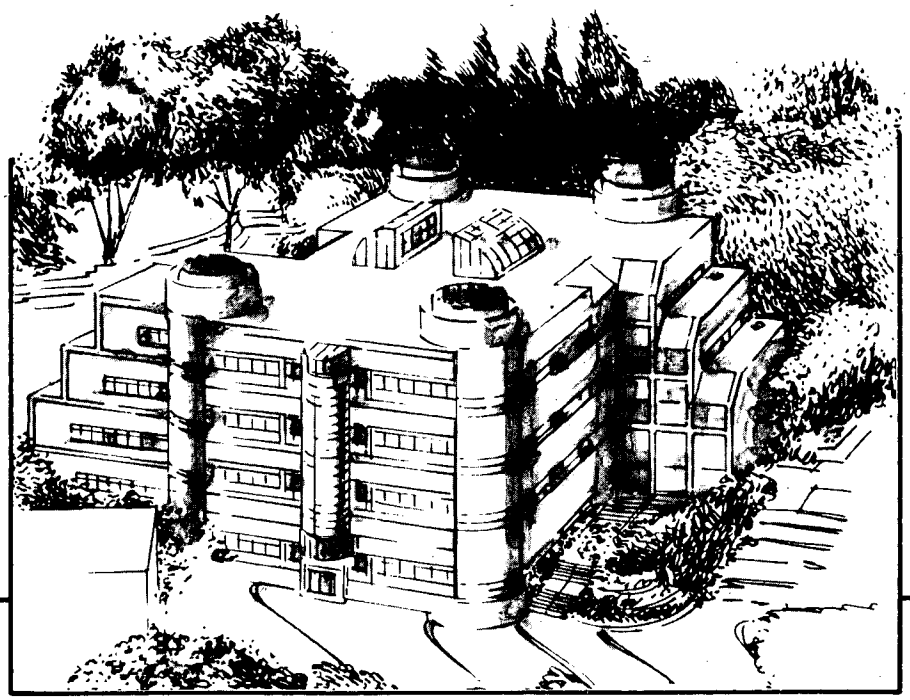

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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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Calculation of Goniometric Functions for Dilute Solutions of Slender Rodlike Molecules in High Peclet Number Shear Flow

by

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SYNOPSIS

An analytic solution to an approximate form of the Fokker-Plank equation of rheological interest has been developed. The derived expression for the orientation distribution function of dilute rod-like molecule solutions in steady simple shear flow applies to the case in which $r \gg \dot{\gamma}/D \gg 1$, where r, $\dot{\gamma}$ and D are the rod aspect ratio, shear rate and rotational diffusivity. Goniometrical functions are also calculated in this limit.

Results compare well with earlier calculations by Schwarz, Hinch & Leal, and Stewart and Sorensen. In particular, the previously reported power law exponent of -1/3 for the asymptotic functional dependence of the goniometrical factors upon $a = \dot{\gamma}/D$ (the rotational Peclet number) is confirmed by the present calculation.

INTRODUCTION

Recent years have witnessed a surge of interest in molecular composites consisting of rigid rod-like macromolecules in amorphous polymeric matrices. These systems hold much promise as engineering materials that exploit both the properties of rigid-rod and flexible coil-like polymers [1].

Problems remain, however, in understanding the thermodynamics and rheology of such potentially morphologically complex systems. Matrix viscoelasticity and microenvironmental topology can significantly affect the rheology of these blends. For example, rotational diffusivity of the rod-like molecules is expected to undergo an abrupt transition when the rod length becomes comparable to the average distance between entanglements formed by the matrix molecules (i.e., the "virtual" tube diameter of the surrounding network). For long rods in concentrated polymer solutions, rotation may in fact be accomplished by reptation of either the flexible coils or the rod itself to release the topological constraints. Diffusion times for the rigid molecule rotation are then expected to be much greater than those attainable in dilute (rod) solutions in Newtonian solvents. Practical processing of molecular composites thus often involves rates of deformation that are large compared to any intrinsic orientation relaxation process. In the case of simple shear flow this would imply:

$$a = \dot{\gamma}/D \gg 1 \qquad (1)$$

where a, $\dot{\gamma}$ and D are the rotational Peclet number, the prevailing shear rate and rod rotational diffusivity. As pointed out by Hinch & Leal [2,3] for the case of thin prolate ellipsoids, the conditions $\dot{\gamma}/D \gg 1$ and $r \gg 1$ are not themselves sufficient to uniquely specify a regime of "strong" flow. Indeed,

as shown by Jefferey [4], neutrally buoyant ellipsoids rotate, in shear flow, with a natural frequency $2\pi/T$, the period T being directly proportional to the particle axis ratio r and inversely proportional to the shear rate $\dot{\gamma}$. Moreover, in the case of "strong flow", the ellipsoids closely align around a common orientation orthogonal to the local fluid vorticity axis and parallel to the plane of shear. This defines, in the orientation phase space, a high concentration region in which both convection and diffusion are important. Hinch and Leal termed this region "the boundary layer" [2,3]. The extent, Δ, over which it protrudes in the phase space is uniquely determined by a balance between advection and diffusion. Δ has been shown to scale as $(\dot{\gamma}/D)^{-1/3}$ [3,5,6].

A third condition is then necessary in order to specify Brownian motion which, although unimportant outside the "layer", still plays a significant role inside it. The angular diffusion time within the highly populated region must be smaller than the hydrodynamic period T, i.e., $T \gg \Delta^2/D$ or equivalently $r^3 \gg \dot{\gamma}/D$. If this is the case, then the ellipsoids kinematically behave as infinitely thin rods and the only driving force capable of "expelling" them out of the layer is Brownian motion.

As $r \to \infty$ Jefferey's equations for the motion of the ellipsoid reduce to:

$$\dot{\underset{\sim}{p}} = (\underset{\approx}{I} - \underset{\sim}{p}\underset{\sim}{p}) \cdot (\underset{\approx}{K} \cdot \underset{\sim}{p}) \qquad (2)$$

Here, as usual, $\underset{\sim}{p}$ is a unit vector parallel to the rod major axis, $\underset{\approx}{K} = \underset{\sim}{\nabla}\underset{\sim}{V}$ is the local fluid velocity gradient tensor, and $\underset{\approx}{I}$ is the identity tensor. Note that Eq.2 can be derived by purely kinematic arguments. It states that (in the absence of external torques) "long" rods are unable to rotate by "cutting" the surrounding medium. The only relative motion allowed is "slippage" of the

fluid along the rod axis with a velocity:

$$\underset{\sim}{V} = s\ (\underset{\sim}{V} \cdot \underset{\sim}{p})\ \underset{\sim}{p} = (\underset{\approx}{K} : \underset{\sim}{p}\underset{\sim}{p})\ \underset{\sim}{p}\ s \tag{3}$$

the scalar s $(0<s<\frac{L}{2})$ specifies the position relative to the rod center. (L is the length of the rod). The rod angular velocity must, then, be equal to the local fluid rate of rotation:

$$\dot{\underset{\sim}{p}} = \frac{\underset{\sim}{V} - \underset{\sim}{V}}{s} = (\underset{\approx}{I} - \underset{\sim}{p}\underset{\sim}{p}) \cdot (\underset{\approx}{K} \cdot \underset{\sim}{p}) \tag{4}$$

An important consequence of the limiting behavior described by Eq.2 is that the purely kinematic character of the equations of motion implies their complete independence of the specific nature of the surrounding fluid. In other words, provided that $r^3 >> \dot{\gamma}/D >> 1$, Eq.2 remains the same whether or not the matrix is Newtonian. Hence (when any possible dependence of D upon matrix morphology is excluded) the Fokker-Plank equation describing the instantaneous orientational state of an ensemble of (dilute) rigid-rod molecules in a Newtonian solvent, should be exactly the same (and hence yield the same solution) as the one describing an equivalent system of rods in a medium comprising both large coil-like and low molecular weight molecules (the difference between the two cases would manifest itself in the values assumed by D).

Rheological characterization of dilute solutions of axisymmetric particles in Newtonian solvents has been a very active area during the past seven decades. As a result the pertinent literature is quite abundant and sometimes confusing, expecially from the notational point of view. An excellent article by Brenner [7] synthesized all major theoretical achievements in the field, providing simultaneously explicit results for rheological

quantities and a unified framework for analysis from the hydrodynamic viewpoint. In the following we shall often refer to Brenner's article for comparison of our results with those by other investigators.

In the general context of Brenner's paper our work stands as "the intermediate case" [3,7]. Solution of the Fokker-Plank equation relative to this limit has been considered by several authors. The objective was to predict the three goniometric factors $\langle \sin^2\theta \sin^2\phi + \cos^2\theta \rangle$, $\langle \sin\theta \cos\theta \sin\phi \rangle$ and $\langle \cos^2\theta - \sin^2\theta \sin^2\phi \rangle$ which are necessary for the calculation of rheological and rheooptical properties [7].

The first attempt to solve a simplified diffusion equation was made by Burgers [5]. Indeed he was the first investigator to succeed in the formulation of a "boundary layer " problem. His analysis demonstrated the existence of the "dense" phase space region and gave its scaling laws. No satisfactory solution, however, was obtained for the resulting differential equation, which was solved by an approximate procedure akin to orthogonal collocation.

Another approximate procedure to determine the orientation distribution function was later adopted by Schwarz [7]. By partial integration of the original P.D.E. he obtained an O.D.E. for a "one-angle pre-averaged" distribution function. An analytical solution was obtained. However, as a result of the pre-averaging approximation just two of the three goniometric factors could be calculated, leaving the third undetermined.

The numerical scheme of Scheraga et. al. [8,9], for axisymmetric spheroids covered the axis ratio range $\infty > r > 1$. The work yielded valuable and accurate results for $60 > a > 0$. The highest value of a explored was 200; the author did not feel confident with any of the results for $a > 60$. Stewart and Sorensen [10] examined the case $r = \infty$ and $\infty > a > 0$. They successfully

obtained an analytic solution in terms of a series expansion of spherical harmonics. The a-dependent coefficients were evaluated by the Galerkin method of weighted residuals. The number of terms required to assure convergence was found to grow rapidly with a for $a>1$. Also a truncated series of N terms required the evaluation of $(N/2+1)^2$ integrals. For example, convergence within four digits of the various stresses at a=180 required N=22 and a corresponding number of 144 integrals. Because of the large number of integrals to be determined the calculations had to be performed numerically. For a greater than 180 the series was constantly truncated at 22 terms. The authors neither advanced any justification regarding their decision, nor discussed the possibility of systematic errors introduced by the truncation. We will confirm the accuracy of their results in the "high a" region of interest.

A further attempt to solve numerically for the distribution function was made by Hinch & Leal [2,3]. Two different numerical schemes, one by finite difference and the other by finite element were employed. The objective was that of determining and matching numerically two asymptotic solutions for the orientation distribution function: the "inner" solution corresponding to the "dense layer" itself, and the "outer" solution valid in regions of the phase space "far" from the high concentration zone. In spite of considerable efforts the authors were only able to obtain estimates for the numerical coefficients in the power law expressions of the goniometrical factors [7].

Following Hinch and Leal, we solve the diffusion equation in two distinct phase space regions: the high concentration "dense layer" and the external low density region. Analytic expressions are derived in both domains and then matched to yield a "global" solution. Although analytic solutions are obtained, complexity of the averaging integral's kernels does not allow for explicit closed-form results for the goniometric factors, which are evaluated by numerical means.

THEORY

Model development is subject to the following assumptions:

(1) As the rods do not interact with each other we are concerned with the case $\Phi r^2 << 1$, Φ being the rods' hard-core volume fraction, and r their aspect ratio. (We consider a monodisperse system).

(2) The suspension is homogeneous. The rods' centers of mass are evenly distributed within the physical space.

(3) No external torque-inducing fields act on the system.

(4) Inertia forces are unimportant for both the medium and the suspended particles, which are also neutrally buoyant.

Under these assumptions, the rod orientation is is uniquely described by the orientation distribution function χ, defined as follows. Let dN/N_t be the fraction of rods whose unit vector, $\underline{p}$, lies in the range $[\underline{p},\underline{p}+d\underline{p})$. The orientation distribution function is defined as:

$$\frac{dN}{N_t} = \chi(\underline{p})\ d^2\underline{p} \tag{5}$$

where N_t is the total number of rods. The following restrictions apply to χ:

$$\chi(\underline{p}) = \chi(-\underline{p}) \text{ (symmetry)} \tag{6}$$

$$\int \chi(\underline{p})\ d^2\underline{p} = 1 \quad \text{(normalization)} \tag{7}$$

In Eq.7 the integration is extended to the whole phase (angular) space. With respect to a spherical, phase-space coordinate system Eqs. 5-7 become:

$$\frac{dN}{N_t} = \chi\ (\theta,\Phi)\ \sin\theta\ d\theta\ d\phi \tag{8}$$

$$\chi(\theta,\phi) = \chi\ (\pi-\theta,\ \pi + \phi) \tag{9}$$

$$\int_o^{\pi} \int_o^{2\pi} \chi \sin\theta\ d\theta\ d\phi = 1 \tag{10}$$

Equation 10 stipulates that for an isotropic equilibrium distribution $\chi = 1/4\pi$. In addition to Eqs. 9 and 10 one further constraint must be obeyed:

$$\frac{\partial\chi}{\partial\phi} = 0 \text{ at } \phi = \frac{\pi}{2} \text{ and } \phi = \frac{3}{2}\pi \tag{11}$$

This condition preserves the intrinsic symmetry of the problem as dictated by the specific structure of the flow field (shear flow).

A force balance in the physical space coupled with a conservation statement in the phase space lead to the following modified Fokker-Plank equation for χ:

$$\frac{\partial\chi}{\partial t} = - \underset{\sim}{\nabla}_p \cdot (\chi\ \dot{\underline{p}} - D\ \underset{\sim}{\nabla}_p \chi) \tag{12}$$

where $\partial\chi/\partial t$ and $\dot{\underline{p}}$ denote the time rate of change of χ and $\underline{p}$ respectively, $\underset{\sim}{\nabla}_p$ is the phase space gradient operator, and D is the rotational diffusion coefficient of the rods. Equation 12 states that the local state of orientation changes in time as a result of two competing actions, Brownian motion and hydrodynamic convection.

In the limit of infinite aspect ratio the motion of a rod in a generic, homogeneous flow field can be described by Eq.2 [4,12], which states that no rod-fluid relative motion is possible in any direction orthogonal to the rod major axis. In the case of steady simple shear flow $\partial\chi/\partial t=0$. By choosing as the reference frame the coordinate system illustrated in Fig. 1,we can write:

$$\underset{\approx}{K} \equiv \begin{matrix} 0 & 0 & 0 \\ 0 & 0 & \dot{\gamma} \\ 0 & 0 & 0 \end{matrix} \tag{13}$$

where $\dot{\gamma}$ is the shear rate. Also:

$$(\dot{p})_\theta = \dot{\theta} = \dot{\gamma} \cos^2\theta \sin\phi$$

$$(\dot{p})_\phi = \dot{\phi} = \dot{\gamma} \cot\theta \cos\phi \tag{14}$$

Then Eq. 12 becomes:

$$\frac{\partial}{\partial\theta} \chi \sin\theta \left(a \cos^2\theta \sin\phi - \frac{\partial \ln\chi}{\partial\theta}\right) +$$

$$+ \frac{\partial}{\partial\phi} \chi \sin\theta \left(a \cot\theta \cos\phi - \frac{1}{\sin^2\theta} \frac{\partial \ln\chi}{\partial\phi}\right) = 0 \tag{15}$$

Here again $a = \dot{\gamma}/D$ is the rotational Peclet number [2,3], a measure of the relative importance of convection and diffusion.

Equation 15 subject to 9 - 11, is rather difficult to solve analytically over the whole phase space and for any arbitrary value of the parameter a. Since we are concerned here with the case $r^3 \gg a \gg 1$ in which the distribution function strongly peaks in regions of the phase space where $\dot{p} = 0$, we make use of the following approximations. We divide the angular space into two distinct regions, that outside the "dense" layer, and the layer itself. Specifically the "dense" layer is the equatorial region near $\theta \sim \pi/2$. Here the rods closely align in the fluid velocity direction, and their rotational speed $\dot{p}$ diminishes. Hence, the diffusive term in Eq. 15 becomes significant and must be dealt with explicitly. Outside the "dense" layer, convection is predominant over diffusion. Solution in this region can be facilitated

appreciably by the following procedure. We first define:

$$A = \ln(\tan \frac{\theta}{2}) \tag{16}$$

This new variable allows the transformation of Eq. 15 into the following:

$$\frac{\partial^2 \chi}{\partial A^2} + \frac{\partial^2 \chi}{\partial \phi^2} = a \left[\sin\phi \frac{\tanh^2(A)}{\cosh(A)} \frac{\partial \chi}{\partial A} - \cos\phi \frac{\tanh(A)}{\cosh(A)} \frac{\partial \chi}{\partial \phi} + \right.$$

$$\left. + 3\chi \frac{\sin\phi \tanh(A)}{\cosh^3(A)} \right] \tag{17}$$

Or, in compact notation

$$\nabla^2 \chi = a\, \Omega\, (A, \phi, \chi_A, \chi_\phi, \chi) \tag{18}$$

For large values of a, i.e., the convective term dominating, $\Omega \cong 0$. This leads to the following solution (outlined in Appendix A):

$$\chi = \frac{F(\tan\theta \cos\phi)}{|\cos\theta|^3} \tag{19}$$

where F is an arbitrary function. Note that [$\tan\theta \cos\phi$ = constant] defines the trajectories traced by rod ends rotating in simple shear flow. Function F, therefore mirrors the relative population distribution of rods over these trajectories. The inverse dependence on $|\cos\theta|^3$ arises from the term $(\chi \underset{\sim}{\nabla}_p \cdot \dot{\underset{\sim}{p}})$ (Eq. 12) and reflects the "compressible" nature of the $\dot{\underset{\sim}{p}}$ "flow field". Function F is then uniquely determined by the orientation distribution inside the "dense" layer, and can be found by matching Eq. 2 with the corresponding "inner" solution at the interface of the two regions.

Solution within the dense layer is facilitated by noting that

$\theta \sim \frac{\pi}{2}$, $\sin\theta \sim 1$ and $\cos\theta \sim \frac{\pi}{2} - \theta$. Equation 15 is thus reduced to

$$-\frac{\partial^2\chi}{\partial\delta^2} - \frac{\partial^2\chi}{\partial\phi^2} - \frac{\partial\chi}{\partial\delta} a\delta^2 \sin\phi + \frac{\partial\chi}{\partial\phi} a\delta \cos\phi - 3a\chi\delta \sin\phi = 0 \tag{20}$$

where $\delta = \frac{\pi}{2} - \theta$. If this quantity is normalized by Δ_θ, the dense layer "thickness" in the θ direction, we obtain:

$$-\frac{\partial^2\chi}{\partial\eta^2} - \Delta_\theta^2 \frac{\partial^2\chi}{\partial\phi^2} - \frac{\partial\chi}{\partial\eta} \eta^2 \sin\phi \, (a\Delta_\theta^3) +$$

$$+ \frac{\partial\chi}{\partial\phi} \eta \cos\phi \, (a\Delta_\theta^3) - 3\chi\eta \sin\phi \, (a\Delta_\theta^3) = 0 \tag{21}$$

where $\eta = \frac{\delta}{\Delta_\theta}$. Since the convective and diffusive terms must be of comparable magnitude within this region, $(a\Delta_\theta^3)$ must be of the order of unity, i.e., $\Delta_\theta = a^{-1/3}$. Note that the dense layer thickness decreases with increases in the rotational Peclet number, and the quantitative dependence is identical to that found previously by other investigators [2,3,5]. If the second term on the left hand side of Eq. 21 is assumed to be negligible compared with the other terms, the following equation is obtained:

$$-\frac{\partial^2\chi}{\partial\eta^2} - \frac{\partial\chi}{\partial\eta} \eta^2 \sin\phi + \frac{\partial\chi}{\partial\phi} \eta \cos\phi - 3\chi\eta \sin\phi = 0 \tag{22}$$

This equation can be solved by combination of variables. Following conventional similarity-solutions techniques [11], we assume the orientation distribution function to take on the form below :

$$\chi(\eta,\phi) = g(\phi) \, f\big(y(\phi).\eta\big) \tag{23}$$

Upon substitution of Eq. 23 into Eq. 22, subsequent manipulation yields (see

Appendix B for details):

$$\chi(\eta,\phi) = c\, y^3\, f(\eta\, y) \tag{24}$$

where

$$y = \left[\cos\phi(\tan^3\phi + 3\tan\phi + a/2^{\;3/2})^{1/3}\right]^{-1} \tag{25}$$

$$f(u) = \left(1 - u\, e^{-u^3/3} \int_{-\infty}^{u} x\, e^{x^3/3} dx\right) \tag{26}$$

C is a constant to be determined by global normalization (Eq.10). Also note that (with reference to Eq. 23):

$$g = \text{const.}\; y^3 \tag{27}$$

Equations 24 - 26 are valid within the dense layer. In the transition region we assume the following dependence for η:

$$\eta = a^{1/3} \cos\theta \tag{28}$$

Matching of the inner (Eq.24) and outer (Eq.19) solutions is achieved by noting that (see Appendix B):

$$f(u) \rightarrow \frac{\text{constant}}{|u|^3} \quad \text{for large } |u| \tag{29}$$

Hence, in this limit the function χ becomes:

$$\chi(\theta,\phi) = \frac{\text{constant}}{|\cos\theta|^3} \tag{30}$$

which is identical to Eq. 19 if function F is taken to be a constant. In its final form the distribution function is given by:

$$\chi(\theta,\phi) = c\, y^3(\phi)\, f(\eta y) \tag{31}$$

where $y(\theta)$ is described by Eq.25, and:

$$f(u) = \text{given by Eq.26} \quad \text{for} \quad 1.377>u>-2 \tag{32}$$

$$f(u) = \frac{\alpha}{|u|^3} \qquad \text{for} \quad u>1.377 \tag{33}$$

$$f(u) = \frac{\alpha}{(|u| + \beta)^3} \qquad \text{for} \quad u<-2 \tag{34}$$

where $\alpha = 1.931$ and $\beta = 0.79$

In Eqs. 33 and 34 the constant α has been determined by imposing continuity of f and its first derivative (calculated from Eq.33) at the point $u = 1.377$ where the second derivative of f (as calculated from Eq.19) vanishes. With the choice $\beta = 0.79$, Eq. 34 matches Eq. 26 within a few percent for $u<-2$. Figures 2 and 3 show functions y and f within the dense layer (Eqs.25 and 26). While function y is symmetric with respect to $\phi = \frac{\pi}{2}$ (Fig. 2) distinct asymmetry is revealed in the plot of f versus $u = \frac{\cos\theta}{\Delta_\theta}\, y$ (Fig. 3). The orientation distribution favors $u>0$ in the dense layer, i.e., regions of the upper hemisphere are more populated. As seen in Fig. 3, $\theta = \frac{\pi}{2}$ (or the equator) is an unstable equilibrium point. As soon as the rods move out of this plane by Brownian diffusion towards the lower hemisphere ($u<0$), convective forces imposed by the surrounding fluid rapidly carry the rods away from $\theta = \frac{\pi}{2}$. However, on the u-positive side, any Brownian motion tilting the rods from their equilibrium alignment is countered by restoring

convective forces.

Once the distribution function is specified, the material functions can be calculated. The relationships between these quantities and the goniometrical factors are given in great detail in Refs. [3] and [7], and will not be repeated here.

The goniometrical functions are here defined as follows:

$$G_1 = \langle \sin^2\theta \sin^2\phi + \cos^2\theta \rangle$$

$$G_2 = \langle \sin\theta \cos\theta \sin\phi \rangle$$

$$G_3 = \langle \cos^2\theta - \sin^2\theta \sin^2\phi \rangle \tag{35}$$

Note that given our choice of coordinate system the kernels in Eq.35 differ from those published in Ref.[7]. Specifically, denoting the coordinate set adopted by Brenner by (x',y',z') and our frame of reference by (x,y,z), we have:

$$x = -z'$$

$$y = y' \tag{36}$$

$$z = x'$$

or

$$\sin\theta \cos\phi = -\cos\theta'$$

$$\sin\theta \sin\phi = \sin\theta' \sin\phi'$$

$$\cos\theta = \sin\theta' \cos\phi' \tag{37}$$

Given the complexity of the kernels in Eq. 35 the integrations had to be performed numerically. A simple bidimensional Simpson routine was adopted. However, in order to fully capture the features of the strongly peaked

distribution function, the integration domain was divided in four sections. In the $(\cos\theta,\phi)$ plane the boundaries of these domains were determined by:

D1 :
$$\frac{5}{a^{1/3}} \leq \cos\theta \leq 1$$
$$\frac{\pi}{2} - \frac{6}{a^{1/3}} \leq \phi \leq \frac{\pi}{2}$$

D2 :
$$-1 \leq \cos\theta \leq -\frac{5}{a^{1/3}}$$
$$\frac{\pi}{2} - \frac{6}{a^{1/3}} \leq \phi \leq \frac{\pi}{2}$$

D3 :
$$-1 \leq \cos\theta \leq 1$$
$$0 \leq \phi \leq \frac{\pi}{2} - \frac{6}{a^{1/3}}$$

D4 :
$$-\frac{5}{a^{1/3}} \leq \cos\theta \leq \frac{5}{a^{1/3}}$$
$$\frac{\pi}{2} - \frac{6}{a^{1/3}} \leq \phi \leq \frac{\pi}{2} \qquad (38)$$

Since the results were practically unaffected by the inclusion of regions D1 and D2, the integrations were limited to D3 and D4 in order to minimize computation time. On an IBM PC-XT this resulted in a reduction of computing time from three hours to about one hour for each set of (G1,G2,G3) at every a.

RESULTS AND DISCUSSION

Figures 4,5,6 show the results of the present calculation. For comparison purposes the figures include curves previously obtained by Scheraga and

Stewart and Sorensen. Good agreement exists for G1 and G3 with the asymptotic power-law solutions obtained by Stewart and Sorensen, the maximum deviation being less than 5%. The second gonoimetrical factor, G2, (Fig.5) deviates appreciably from the corresponding "exact" solution by Stewart and Sorensen for relatively "small" values of the Peclet number, converging asymptotically as $a \to \infty$. This discrepancy is probably due to the neglect of the term $\frac{\partial^2 \chi}{\partial \phi^2}$ in Eq. 21. Another possible source of error could be the linearization of the trigonometric functions implemented in Eq.15 to obtain Eq.22. Indeed the dense layer thickness in the θ direction, Δ_θ, scales as $a^{-1/3}$. This, for a = 1000 would give an overall dense layer thickness of ~ 0.2, which is about 10% of $\pi/2$.

Once the goniometric functions are computed, conventional rheological properties such as viscosity and normal stress coefficients can be easily determined if the medium is purely viscous.

Since the validity of the present analysis is unaffected by the specific nature of the solvent (or matrix) under consideration, the results presented here will be employed in a future paper to model the effect of matrix viscoelasticity on the behavior of molecular composites. For purely viscous matrices the hydrodynamic frictional drag coefficient, ξ , is time and history invariant. For rods dissolved in polymeric solutions or even melts, the flexible coils may interact with a given rod by anchoring themselves at selected points. Fluid slippage may in fact proceed by distending the coils while displacing the contact points simultaneously. This process is best described by a viscoelastic constitutive equation, such as the Maxwell equation:

$$\lambda \frac{d}{dt}\left(dF(\delta)\right) + dF(\delta) = -V \quad \xi d\delta \tag{5}$$

where λ is the relaxation time characteristic of local coil deformation, dF

the incremental hydrodynamic force acting on a differential rod segment $d\delta$, and V the relative velocity at rod fluid interface defined by Eq. 3. Note that only the magnitude of the force is computed in this manner. The direction of the force can, as a first approximation, be assumed to coincide with the rod orientation, a point worth further examination. Equation 39 properly reduces to the viscous case when $\lambda = 0$. Complications remain, as the rod orientation evolves with time while the local force develops. The solution to this problem will constitute a major portion of an upcoming publication.

Acknowledgment

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. The problem of molecular composite processing was brought to our attention by Dr. W.F. Hwang of the Dow Chemical Company. Financial contribution from Dow to this research program is greatly appreciated.

Appendix A

In this section we obtain an approximate solution of Eq. 15 (see text) in convection dominated regions. We begin by implementing the following change of variable:

$$A = \ln(\tan(\theta/2)) \tag{A1}$$

Then for:

$$0 \leq \theta \leq \pi \quad \text{or} \quad -\infty < A < \infty \tag{A2}$$

$$\cos\theta = -\tanh(A) \quad \text{and} \quad \sin\theta = \frac{1}{\cosh(A)}$$

Thus allowing Eq.8 to be written as:

$$\frac{\partial^2\chi}{\partial A^2} + \frac{\partial^2\chi}{\partial\phi^2} = a\Big(\sin\phi\,\frac{\tanh^2(A)}{\cosh(A)}\,\frac{\partial\chi}{\partial A} +$$

$$- \cos\phi\,\frac{\tanh(A)}{\cosh(A)}\,\frac{\partial\chi}{\partial\phi} + 3\chi\,\frac{\tanh(A)\,\sin\phi}{\big(\cosh(A)\big)^3}\Big) \qquad \text{(A3)}$$

For a >> 1, in regions of strong convection, the term on the right-hand side of Eq. A3 dominates. We have then:

$$\tanh(A)\,\frac{\partial\chi}{\partial A} + \cot\phi\,\frac{\partial\chi}{\partial\phi} + \frac{3\chi}{(\cosh(A))^2} = 0 \qquad \text{(A4)}$$

Solution of Eq. A4 is appreciably simplified if we define:

$$\omega \equiv \ln(\sinh(A))$$

$$\lambda \equiv \ln(\cos\phi)$$

$$\psi \equiv \ln\chi \qquad \text{(A5)}$$

With this change of variables Eq. A4 becomes:

$$\frac{\partial\Psi}{\partial\omega} + \frac{\partial\Psi}{\partial\lambda} + \frac{3}{1 + e^{2\omega}} = 0 \qquad \text{(A6)}$$

This equation is easily solved by the method of characteristics [11]. The general solution is:

$$\Psi = \frac{3}{2}\,\ln\Big(\frac{1 + e^{2\omega}}{e^{2\omega}}\Big) + L\,(\omega - \lambda) \qquad \text{(A7)}$$

where L is an arbitrary function of $(\omega - \lambda)$. In the (θ,ϕ) space Eq. A7 becomes:

$$\chi = \frac{F(\tan\theta \cos\phi)}{|\cos\theta|^3} \tag{A8}$$

where function F is uniquely determined by the orientation distribution inside the dense layer (see text and Appendix B).

Appendix B

Below is a sketch of the solution procedure for the following equation:

$$\frac{\partial^2\chi}{\partial\eta^2} + \frac{\partial\chi}{\partial\eta}\,\eta^2\sin\phi - \frac{\partial\chi}{\partial\phi}\,\eta\cos\phi + 3\chi\,\eta\sin\phi = 0 \tag{B1}$$

Due to the symmetry of χ, we restrict ourselves to the integration domain defined by $0<\theta<\pi$, $0<\phi<\pi/2$.

We seek a solution of the form:

$$X(\eta,\phi) = g(\phi)\ f\ (u)$$

$$u = \eta\ y(\phi) \tag{B2}$$

where functions g, y, and f are to be determined. Let the superscripts <'> and <"> denote respectively the first and second derivative of the functions g, y or f. Substitution of Eq. B2 into Eq. B1 after some rearrangement gives:

$$f'' + f'\ u^2\left(\frac{y\sin\phi - y'\cos\phi}{y^4}\right) + f\ u\left(\frac{3\,g\sin\phi - g'\cos\phi}{g\ y^3}\right) = 0 \tag{B3}$$

Since g and y are only functions of ϕ, we impose:

$$(y'\cos\phi - y\sin\phi) = -K_1\ y4 \tag{B4}$$

$$(g'\cos\phi - 3\, g\, \sin\phi) = -\, K_2\, g\, y^3 \tag{B5}$$

Where K_1 and K_2 are constants.

Then,

$$f'' + K_1\, f'\, u^2 + K_2\, f\, u = 0 \tag{B6}$$

Dividing Eq. B4 by $(K_1\, y)$, Eq. B7 by $(g\, K_2)$, and equating the resulting expressions, we obtain:

$$\frac{d}{d\phi}\left(\ln(y) - \frac{K_1}{K_2}\ln(g)\right) = \tan\phi\left(1 - 3\frac{K_1}{K_2}\right) \tag{B7}$$

which can be integrated to give:

$$g = K_3\, y^{\left(\frac{K_2}{K_1}\right)} \cos\phi^{\left(\frac{K_2}{K_1} - 3\right)} \tag{B8}$$

where constant K_3 can be incorporated in the overall normalization constant.

Integration of Eq.B4, can be facilitated by the following symmetry condition:

$$\text{at } \phi = \pi/2 \qquad \partial\chi/\partial\phi = 0 \tag{B9}$$

Differentiation of Eq.B2 gives:

$$g'\, f + \eta\, g\, f'\, y' = 0 \qquad \text{at} \qquad \phi = \pi/2 \tag{B10}$$

Since f and f' are independent functions, we require:

$$g' = y' = 0 \quad \text{at} \quad \phi = \pi/2 \tag{B11}$$

The specific structure of Eq. B1 allows us, without any loss of generality, to impose the following condition:

$$y = 1 \text{ at } \phi = \pi/2 \tag{B12}$$

which upon substitution into Eq. B4 yields:

$$K_1 = 1 \tag{B13}$$

Eq. B4 can thus be rewritten as:

$$y' \cos\phi - y \sin\phi = - y^4 \tag{B14}$$

In spite of its strong nonlinearity, Eq. B14 is easily solved by implementing a change-of-variable. Let

$$y = z(\phi)/\cos\phi \tag{B15}$$

which can be substituted into Eq. B14 to give:

$$z' = - z^4 / \cos^4\phi \tag{B16}$$

Solution of Eq. B16 by integration gives:

$$z(\phi) = (\tan^3\phi + 3 \tan\phi + K_4)^{-1/3} \tag{B17}$$

and

$$y(\phi) = [\cos\phi\ (\tan^3\phi + 3\ \tan\phi + K_4)^{\ 1/3}]^{-1} \tag{B18}$$

By requiring g to be finite at $\phi = \pi/2$ we obtain from Eq. B8 :

$$K_2 = 3 \tag{B19}$$

and

$$g(\phi) = K_3\ y(\phi)^3 \tag{B20}$$

Knowledge of the numerical values of K_1 and K_2 allows Eq.B6 to be rewritten as:

$$f'' + u^2\ f' + 3\ u\ f = 0 \tag{B21}$$

The only solution of Eq.B21 which is bounded as $|u|$ approaches infinity is:

$$f(u) = 1 - u\ e^{-\ u^3/3} \int_{-\infty}^{u} t\ e^{\ t^3/3}\ dt \tag{B22}$$

Thus, in its final form the function χ can be written as:

$$\chi = C\ y(\phi)^3\ f(\eta\ y(\phi)) \tag{B23}$$

Here C is a global constant to be determined by normalization, and $y(\phi)$ and f are given by Eqs. B18 and B22 respectively.

Two remarks will be made here. The first concerns the asymptotic behavior of function f. As u, in absolute value, approaches infinity, and f"

becomes negligibly small (i.e., in the convection dominated region) we obtain from Eq. B21:

$$u\, f' \cong -3\, f \qquad \text{for } |u| \to \infty \tag{B24}$$

which upon integration gives:

$$f \cong \frac{\text{constant}}{|u|^3} \qquad \text{for } |u| \to \infty \tag{B25}$$

Then, from Eqs. B23 and B25:

$$\chi \cong \frac{\text{const.}}{|\eta|^3} \qquad \text{for large } |u| \tag{B26}$$

which correctly reproduces the functional form of χ outside the dense layer if we assume η to be given by:

$$\eta = a^{1/3} \cos\theta \tag{B27}$$

The second remark concerns the determination of constant K_4 which appears in Eq. B17. There remains no other feasible boundary condition to determine the numerical value of K_4. The neglect of the second partial derivative of χ in the ϕ direction in Eq. B1 is the cause. We observe, however, that K_4 must be proportional to a, since around $\phi = \pi/2$ ($\cos\phi \cong (\pi/2-\phi)$ and $\sin\phi \cong 1$) Eq.B1 can be "scaled" by the following change of variable:

$$\zeta = a^{1/3}\, \alpha\, (\frac{\pi}{2} - \phi) \tag{B28}$$

where α is an undetermined numerical constant. If

$$K4 = \alpha^3 a \tag{B29}$$

we obtain from Eqs. B18 and B23:

$$\chi \equiv \frac{\text{const.}}{(1 + \zeta^3)} f \left(\eta \frac{1}{(1+ \zeta^3)^{1/3}}\right) \tag{B30}$$

where f is as before given by Eq. B22. Recall that the dense layer thickness in the θ direction is defined by the equation

$$\Delta\eta^* = 1 \qquad \text{or} \qquad a^{1/3} \Delta_\theta = 1 \tag{B31}$$

Then similarly in the ϕ direction :

$$\Delta\zeta^* = 1 \qquad \text{or} \qquad a^{1/3} \Delta_\phi = 1 \tag{B32}$$

Hence,

$$\alpha = \frac{\Delta_\theta}{\Delta_\phi} \tag{B33}$$

Therefore α represents the ratio of the "thicknesses" Δ_θ and Δ_ϕ, and its numerical value does not depend upon a. This suggests that an "independent" estimate of $\Delta_\theta/\Delta_\phi$ would lead immediately to α. Such information can be retrieved from an analysis by Burgers [5]. There, in an attempt to gain information on the position of the maximum of χ , the author solved the scaled diffusion equation in the neigborhood of the maximum. The functional form assumed for χ was Gaussian, with three adjustable parameters, which Burgers estimated by a collocation procedure. Without going into the details of the

solution, we present here the final result obtained for χ, which is:

$$\chi \equiv \text{const. } \exp\left[-\gamma(\eta - \gamma)^2 + \frac{\zeta'^2}{2}\right] \tag{B34}$$

Here $\eta = a^{1/3}(\pi/2-\theta)$, $\zeta' = a^{1/3}(\pi/2-\phi)$, and γ is a constant whose numerical value for slender rods is very close to unity. Equation B34 around $\eta = 1$, $\zeta' = 0$ can be approximated by:

$$\chi \simeq \text{const. } (1-(\eta-1)^2)\,(1-\zeta'^2/2) \tag{B35}$$

By estimating the values of η and ζ' which give $\chi = 0$, we obtain:

$$\Delta\eta = 1 \quad \text{and} \quad \Delta\zeta' = \sqrt{2} \tag{B36}$$

or

$$\frac{a^{1/3}\Delta_\theta}{a^{1/3}\Delta_\phi} = \frac{\Delta_\theta}{\Delta_\phi} = 1/\sqrt{2} \tag{B37}$$

Thus,

$$\alpha = 1/\sqrt{2} \tag{B38}$$

and

$$K_4 = a\,2^{-\frac{3}{2}} \equiv 0.354\ a \tag{B39}$$

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FIGURE CAPTIONS

Fig. 1 Coordinate system used to define the rod orientation. $\underset{\sim}{V}$ denotes the surrounding fluid velocity field. $\underset{\sim}{p}$ is a unit vector parallel to the rod major axis.

Fig. 2 The function $y(\phi)$ plotted for three different values of the rotational Peclet number, a. As shown in the text (Eq.25) $y(0) = \sqrt{2}/a^{1/3}$. It can be seen that as a increases the rods are more likely to be found around $\phi = \frac{\pi}{2}$ or $\phi = \frac{3}{2}\pi$.

Fig. 3 The function f(u) vs. $u = \frac{\cos\theta}{\Delta_\theta} y(\phi)$ (Eq.26). The competition between Brownian diffusion and hydrodynamic convection makes the region $u>0$ ($\cos\theta>0$) more populated than that in which $u<0$ ($\cos\theta<0$). The dense layer region lies within $-1 \lesssim u \lesssim 1$. Outside the dense layer the function follows the behavior prescribed by Eqs. 33 and 34.

Fig. 4 The goniometric functions G_1, G_2 and G_3 vs. a (Eq.35). The solid curves represent the results of the present calculation. The dashed ones correspond to the numerical results of Scheraga (for $a<200$) and Stewart and Sörensen (taken from Ref. [9,10]).

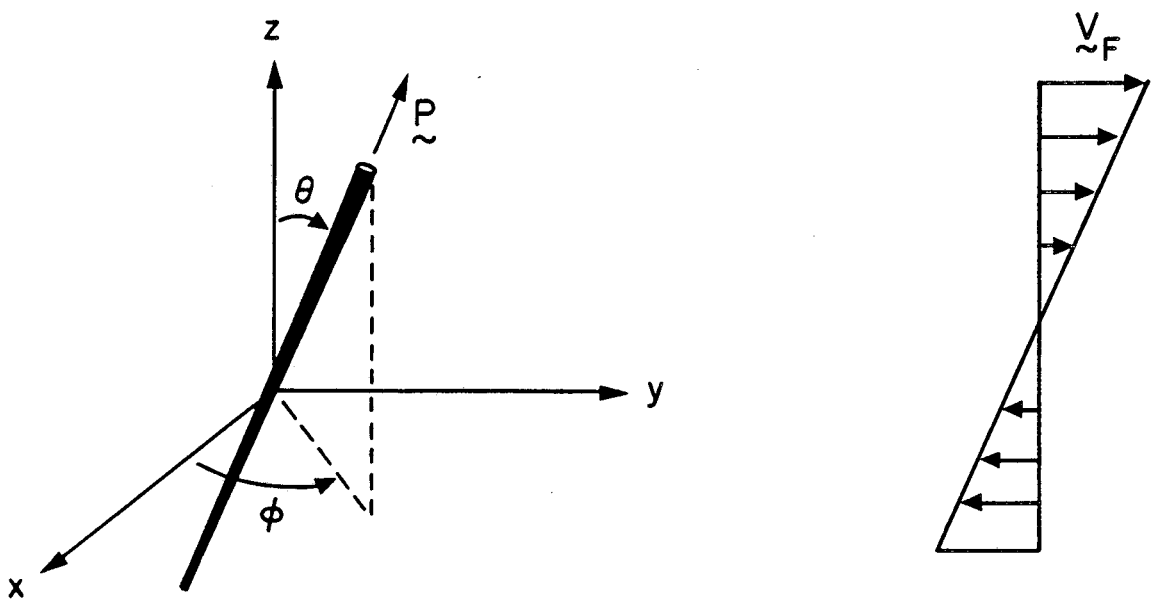


Fig. 1

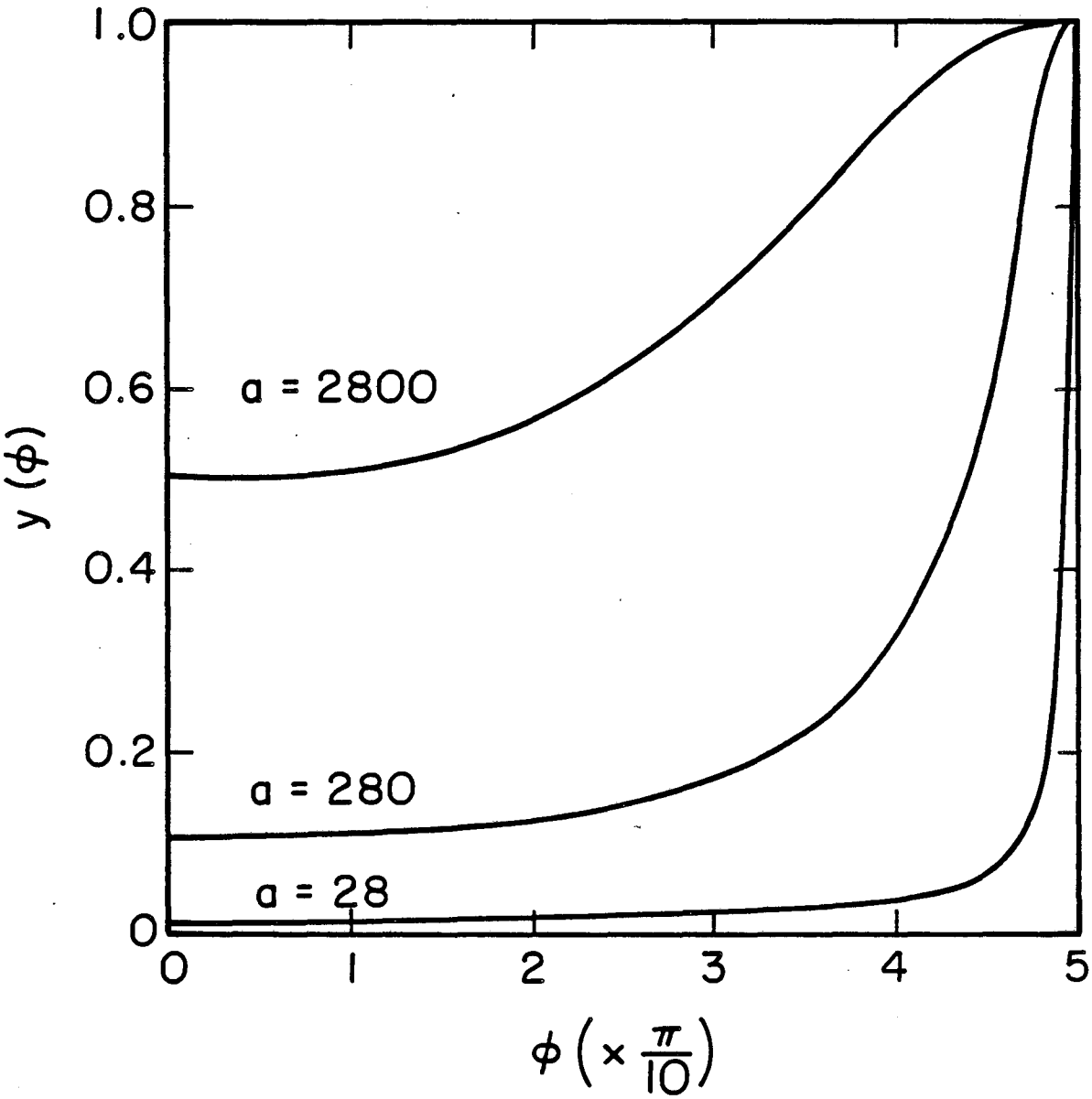


Fig. 2

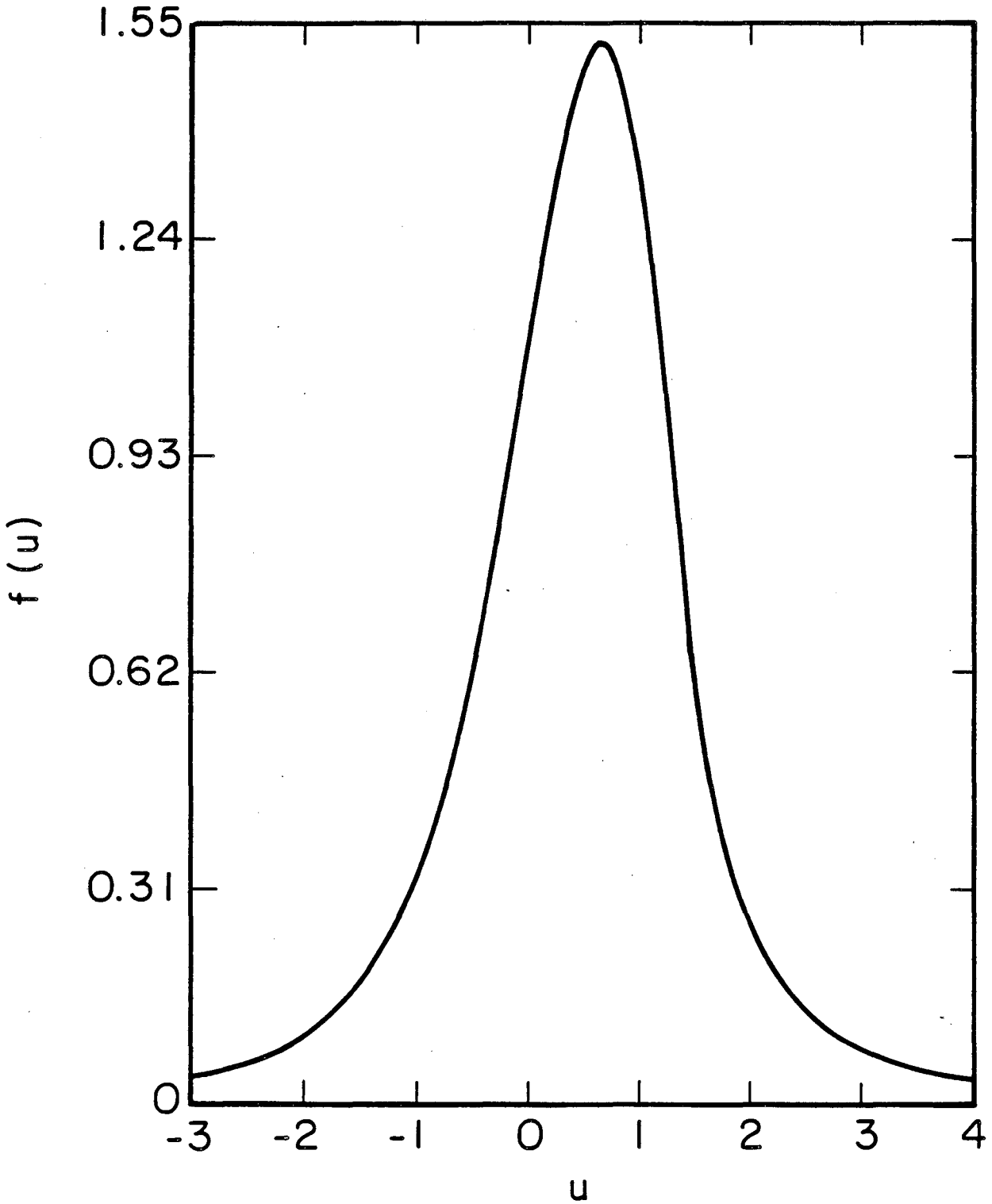
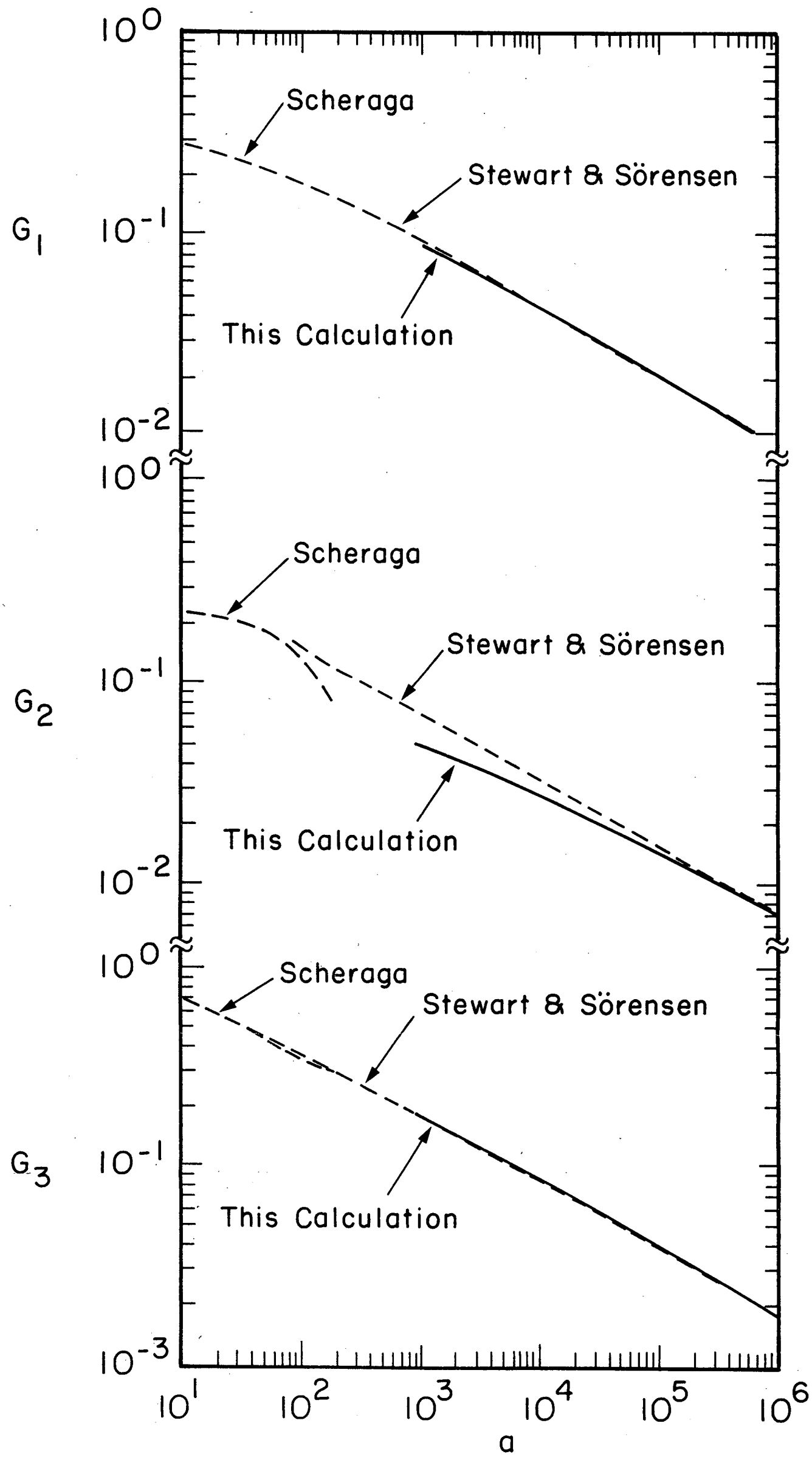


Fig. 3


10^0
10^{-1}
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G_1
Scheraga
Stewart & Sörensen
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G_3
Scheraga
Stewart & Sörensen
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10^1
10^2
10^3
10^4
10^5
10^6
a

Fig 4.

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