

ORIENTATIONAL EFFECT OF THE EXTENSIONAL FLOW FIELD ON SOLUTIONS OF RIGID RODLIKE MACROMOLECULES—DISAPPEARANCE OF THE ISOTROPIC TO NEMATIC PHASE TRANSITION

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Abstract—The effect of steady state uniaxial extensional flow on a solution of rigid rodlike macromolecules is theoretically studied. The mean field theory of Maier and Saupe is extended to cover situations in which the macromolecular solution is subjected to an extensional flow field. It is found that for a given solution a critical flow gradient exists beyond which the first order nematic-isotropic phase transition, which is typical of such solutions in the absence of flow, disappears. A similar result is obtained when the theory of Onsager is applied to the problem. Order parameter as a function of flow gradient is calculated and it is shown that the contribution of flow to the ordering of macromolecules is most significant when the stationary solution is isotropic but close to the transition point.

1. INTRODUCTION

Rigid rodlike macromolecules which appear in both natural and synthetic forms have received widespread attention in recent years. Proteins in helical forms, DNA in its helix configuration, tobacco mosaic virus and a large number of aromatic polyamides belong to this class of macromolecules. Of particular interest are solutions of rodlike polymers in appropriate solvents. Onsager (1949) showed that such solutions can exhibit anisotropic phases at relatively low solute concentrations. The anisotropic phase is characterized by a high degree of macromolecular orientation and the steric repulsion or excluded volume effect can be solely responsible for the existence of this ordered phase. On the technological facet, fibers with exceptional mechanical properties have been spun from solutions of rodlike macromolecules; *Nomex* (marketed by Dupont), *Conex* (by Teijin, Japan), *Fenilon* (by the Soviet Union), and *Kevlar* (by Dupont), all introduced in the late 1960s and early 1970s, are but a few examples of such commercially produced fibers. The high tensile strength of fibers has been attributed to the large degree of macromolecular orientation.

In addition to the excluded volume effect, the presence of external fields can affect the degree of orientation or anisotropy of a macromolecular solution. The frictional forces between the solvent and the solute molecules created in a flow with nonzero velocity gradient, for example, can induce changes in the solution properties. In particular, the uniaxial extensional flow, an example of which is shown in figure 1 and which may be used to represent the flow of spinning dope between the spinneret and the take-up device in a fiber spinning process, can contribute significantly to the orientation of rodlike macromolecules along the elongation axis (Denson 1973; Marrucci 1975; Petrie 1979). An increase of the stretch factor from 1.9 to 5.11 in a typical experiment has reportedly reduced the average orientation angle from 37° to 22°, resulting in a tenacity of 11,000 bar in place of 5,000 bar (Kwolek *et al.* 1977).

Experimental investigations of polymeric solutions undergoing extensional flow have been reported in the literature (Jeffrey & Acrivos 1976; Reher & Karner 1980; Peng & Landel 1980). Both the "four roller" and the "tubeless siphon" have been used to simulate the extensional flow. For the most part, however, these experiments have been concerned with flexible macromolecules and little, if any, data on the extensional flow behavior of rodlike molecules is available at the present time. On the theoretical side, the effect of extensional flow on dilute solutions of rodlike macromolecules has been fully investigated (Bird *et al.* 1977). As for the

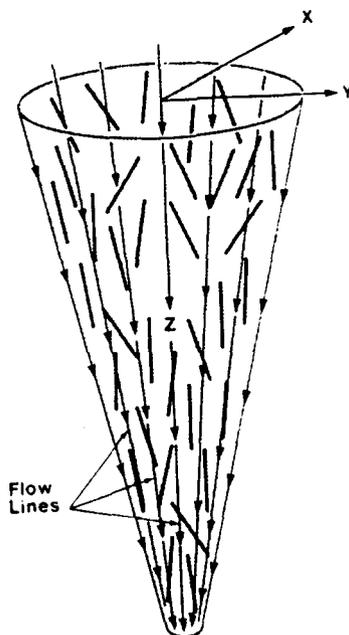


Figure 1. A solution of rigid rodlike macromolecules undergoing uniaxial extensional flow in the Z direction. (Examples of such flow are the flow of spinning dope after the spinneret holes and the flow of a tubeless siphon.)

concentrated regime, Flory's lattice theory has been extended to include the effect of extensional flow (Marrucci & Ciferri 1977). This work has shown that for a given macromolecular solution a critical flow gradient exists beyond which no concentration range can be found in which the phase separation would occur.

The goal of the present paper is to extend two other existing theories of concentrated solutions to include the effect of extensional flow. These are the mean field theory of Maier & Saupe (1959 & 1960) and the theory of Onsager (1949). The concentration range we will be concerned with is the one to which the theory of Onsager can be applied. This regime is sometimes referred to in the literature as the semi-dilute regime. In section 2 a brief account of the effect of flow on dilute solutions is given. Mean field theory in the presence of flow is discussed in section 3, while application of Onsager's method to the problem is the subject of section 4. Section 5 is devoted to some general remarks and conclusions.

2. ORIENTATIONAL EFFECT OF THE EXTENSIONAL FLOW FIELD ON DILUTE SOLUTIONS OF RIGID RODLIKE MACROMOLECULES

In the cartesian coordinate system (X, Y, Z) a uniaxial, homogeneous elongational flow is characterized in the steady state by the following constant velocity-gradient tensor (Petrie 1979):

$$\nabla v = \begin{bmatrix} -0.5\gamma & 0 & 0 \\ 0 & -0.5\gamma & 0 \\ 0 & 0 & \gamma \end{bmatrix} \quad [2-1]$$

where the elongation direction is the Z axis and the rate of elongation is γ (figure 1). While this flow field tends to orient the rodlike solute molecules in the direction of the Z axis, Brownian motion of the much smaller solvent molecules prefers the random distribution of spatial orientations. The competition between these forces results in an orientational distribution

function $\psi(\theta)$ which must satisfy the following differential equation (Bird *et al.* 1977):

$$d/d\theta [D \sin(\theta)(d/d\theta)\psi(\theta) + 3\gamma \cos(\theta) \sin^2(\theta)\psi(\theta)] = 0. \quad (2-2)$$

In this equation θ is the angle between the long axis of the rodlike macromolecules and the Z axis; $\psi(\theta) \sin(\theta) d\theta$ is the probability of finding a given macromolecule in the range between θ and $\theta + d\theta$; and D is the rotational diffusion constant. In general, we can write

$$D = KT/\zeta \quad (2-3)$$

where K is the Boltzmann constant; T is the absolute temperature of the solution; and ζ is a parameter whose value depends on the shape of macromolecules as well as on the nature of their hydrodynamic interaction with the solvent. Although approximate analytical expressions for ζ exist in the literature (Harrington 1964), we regard it here as a phenomenological parameter whose numerical value should be determined experimentally.

The solution to [2-2] can be written as

$$\psi(\theta) = \frac{\exp[(\zeta\gamma/KT)P_2(\cos\theta)]}{\int_0^1 \exp[(\zeta\gamma/KT)P_2(\cos\theta)] d(\cos\theta)} \quad (2-4)$$

where $P_2(\cos\theta) = 0.5(3\cos^2\theta - 1)$ is the second Legendre polynomial, and the integral in the denominator is simply a constant normalizing factor.

The average value of $P_2(\cos\theta)$, denoted by $\langle P_2 \rangle$, is usually used as an order parameter for the system (Priestley *et al.* 1975). Knowing the orientational distribution function from [2-4], we have calculated the order parameter for a dilute solution of rodlike macromolecules undergoing extensional flow. The plot of $\langle P_2 \rangle$ vs $(\zeta\gamma/KT)$ is shown in figure 2 where, as expected, the order parameter is seen to be an increasing function of elongation rate γ . As $\gamma \rightarrow 0$ the order parameter vanishes and therefore the orientation of rods becomes totally random, while as $\gamma \rightarrow \infty$ the order parameter approaches unity which corresponds to a complete alignment of macromolecules in the elongation direction of the flow field.

3. ORIENTATIONAL EFFECT OF THE EXTENSIONAL FLOW FIELD ON SEMI-DILUTE SOLUTIONS OF RIGID RODLIKE MACROMOLECULES: MEAN-FIELD THEORY

Semi-dilute solutions of rigid rodlike macromolecules are known to exhibit nematic order even in the absence of external orienting fields (Onsager 1949; Flory 1956). Order in the nematic state is the result of a compromise between translational and rotational entropies whereby the greater freedom of lateral motion due to the near parallel orientation of macromolecules compensates for their rather severely restricted freedom of rotation. The temperature-induced transition from isotropic to nematic state in these solutions can be best described by the mean field theory of Maier & Saupe (1959-60), in which the effect of neighboring rods on a test rod is cast in a potential field to which the test rod is subjected. Let θ denote the angle between the long axis of the test rod and the nematic director. Then, in its simplest version, the mean field potential can be written as (Priestley *et al.* 1975).

$$\phi_{in}(\theta) = -\alpha \langle P_2 \rangle P_2(\cos\theta) \quad (3-1)$$

where, as before, $P_2(\cos\theta) = 0.5(3\cos^2\theta - 1)$ and $\langle P_2 \rangle$ is the order parameter. α is a positive constant to be determined experimentally. In the above equation, $\langle P_2 \rangle$ represents the effect of long range order on the test rod and must be determined self-consistently. α signifies the strength of the intermolecular field; although α is known to be an increasing function of solute

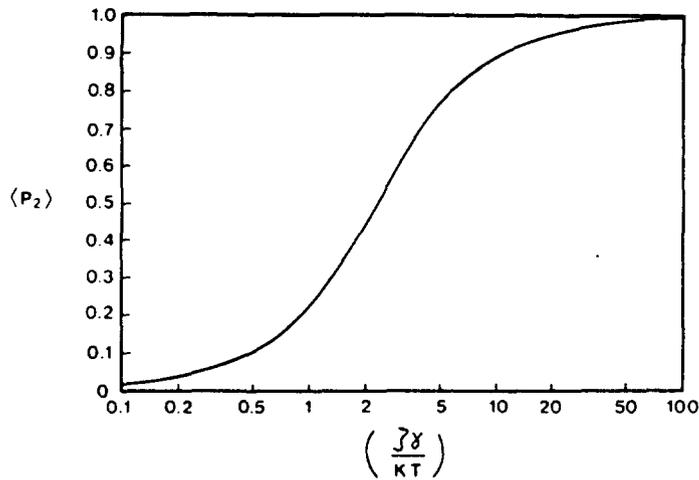


Figure 2. Order parameter $\langle P_2 \rangle$ as a function of flow gradient γ for a dilute solution.

concentration C , the exact relationship between them is as yet unknown. The molecular field theory of Maier and Saupe is, therefore, best suited for the study of situations in which C and consequently α are constants.

To study the effect of extensional flow on a semi-dilute solution, we first notice in [2-4] that the single rod in the dilute regime is subject to the following potential field:

$$\phi_{\text{ext}}(\theta) = -\zeta\gamma P_2(\cos \theta). \quad [3-2]$$

Since in the semi-dilute regime the concentration of macromolecules is not very large, we ignore the effect of disturbance caused by the neighboring rods on the flow field and continue to use ϕ_{ext} in [3-2] as the flow-induced potential field for the test rod. The net potential field can then be written as

$$\phi(\theta) = \phi_{\text{int}}(\theta) + \phi_{\text{ext}}(\theta) = -[\zeta\gamma + \alpha(P_2)]P_2(\cos \theta) \quad [3-3]$$

in which $\langle P \rangle$ must be determined self-consistently, i.e. $\langle P_2 \rangle$ must satisfy the following equation:

$$\langle P_2 \rangle = \frac{\int_0^1 P_2(\cos \theta) \exp[-\phi(\theta)/KT] d(\cos \theta)}{\int_0^1 \exp[-\phi(\theta)/KT] d(\cos \theta)}. \quad [3-4]$$

In reality, the increased concentration of macromolecules in the semi-dilute regime decreases the rotational diffusion constant D , whereas ordering increases this parameter (Doi 1981). Also the hydrodynamic interaction of the neighboring rods with the solvent disturbs the flow field at the sight of the test rod (Bird *et al.* 1977). In a rigorous treatment of the problem these effects must certainly be taken into account in which case terms containing $\gamma\langle P_2 \rangle$ and higher order terms would appear in [3-3]. We feel, however, that the simple potential of [3-3] in its present form contains the essence of the problem and is capable of giving insight without complicating the analysis.

Equation [3-4] has been solved numerically and plots of $\langle P_2 \rangle$ vs (KT/α) for several values of $(\zeta\gamma/\alpha)$ are shown in figure 3. Notice that when the flow gradient is nil the usual first order

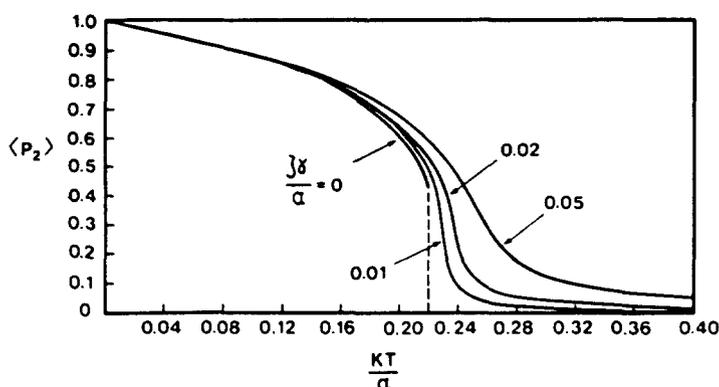


Figure 3. Temperature dependence of the order parameter for a semi-dilute solution undergoing extensional flow with different flow gradients. (If the flow is not too weak, the phase transition disappears.)

transition at $(KT/\alpha) = 0.22019$ is present[†], while when the flow gradient is not exceedingly small (i.e. when $(\zeta\gamma/\alpha) \geq 0.01$), the abrupt transition disappears and the order parameter vs (KT/α) exhibits a smooth behavior.

Figure 4 shows plots of $\langle p_2 \rangle$ vs $(\zeta\gamma/\alpha)$ for several values of (KT/α) . One can deduce from these curves that when the solution is isotropic and far from the transition point (i.e. when $(KT/\alpha) \gg 0.22$), relatively large flow gradients are required for the achievement of any significant degree of orientation. When the solution is anisotropic and, again, far from the transition point (i.e. when $(KT/\alpha) \ll 0.22$), the orientation is already there and there is not much that the flow gradient can do about it. It is therefore around the transition point, and specially in the case of isotropic solutions, that the elongational flow has its most pronounced effect; the curve for $(KT/\alpha) = 0.24$ in figure 4 shows the dramatic increase of the order parameter at moderate values of the flow gradient.

4. ORIENTATIONAL EFFECT OF THE EXTENSIONAL FLOW FIELD ON SEMI-DILUTE SOLUTIONS OF RIGID RODLIKE MACROMOLECULES: THEORY OF ONSAGER

Onsager (1949) studied the statistical mechanics of semi-dilute solutions of rodlike macromolecules and derived an expression for the solution's free energy with due consideration given to the steric hindrance effect. Given two rods with orientations defined by the solid angles Ω and Ω' , respectively, the mutual excluded volume $V_{ex}(\Omega, \Omega')$ was defined as the volume of region into which the center of mass of one macromolecule could not penetrate due to the presence of the other macromolecule. Onsager showed that in order to study the semi-dilute regime one must include in the expression for the free energy of ideal solution a correction term containing $V_{ex}(\Omega, \Omega')$. Unlike the mean field theory, Onsager's theory is capable of describing the state of the system in terms of the concentration C of macromolecules. However, the temperature dependence of $V_{ex}(\Omega, \Omega')$ is as yet unknown and Onsager's theory is therefore best suited for the study of systems at fixed temperature and varying concentration.

Although in his study Onsager did not consider the effect of external fields, it is straight forward to generalize his results to include such effects. Neglecting a constant additive term, the generalized free energy of a test rod in the Onsager problem can be written as

$$F = KT \int \psi(\Omega) \ln [\psi(\Omega)] d\Omega + 0.5 CKT \iint \psi(\Omega) \psi(\Omega') V_{ex}(\Omega, \Omega') d\Omega d\Omega' + \int \psi(\Omega) \phi_{ext}(\Omega) d\Omega \quad [4-1]$$

where, as before, $\psi(\Omega)$ is the orientational distribution function, $\phi_{ext}(\Omega)$ is the external potential field, and C is the number of rods per unit volume. $\psi(\Omega)$ must minimize the above free energy.

[†]To be precise we must mention that the transition is, in fact, a feature of thermotropic liquid crystals. Polymeric solutions, in contrast, exhibit phase separation in a narrow region around $(KT/\alpha) = 0.22$. This distinction has been ignored in our discussions.

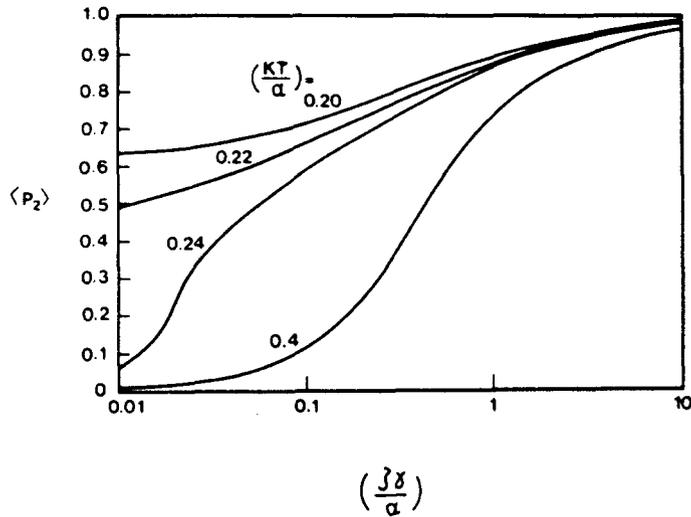


Figure 4. Flow gradient dependence of the order parameter of a semi-dilute solution at different temperatures. (Note that at $(KT/\alpha) = 0.24$, where the solution is isotropic and only slightly above the critical temperature, the elongational flow is most effective.)

The exact analytical solution of the Onsager problem does not exist; nevertheless, it has been solved numerically (Lasher 1970). There is a case, however, where a simplifying assumption reduces the problem to one that is readily solvable and yet the solutions maintain the general features of the more elaborate version. In the so called Zwanzig model (Zwanzig 1963) the orientation of rods is confined to the three principal directions of space; namely, the rods can lie only along the X, Y and Z directions. Equation [4-1] for the Zwanzig model can be written as a function of the order parameter $\langle P_2 \rangle$ as follows:

$$3F/KT = (2\langle P_2 \rangle + 1) \ln(2\langle P_2 \rangle + 1) + 2(1 - \langle P_2 \rangle) \ln(1 - \langle P_2 \rangle) - C(V_{\perp} - V_{\parallel})\langle P_2 \rangle^2 - 3(\zeta\gamma/KT)\langle P_2 \rangle \quad [4-2]$$

V_{\perp} is the excluded volume when the rods are perpendicular to each other and V_{\parallel} is the excluded volume when the rods are parallel.

Figure 5 shows plots of free energy vs $\langle P_2 \rangle$ for several values of $C(V_{\perp} - V_{\parallel})$. These curves belong to the special case of $(\zeta\gamma/KT) = 0$, the case of vanishing flow gradient. It is observed that

- (i) When $C(V_{\perp} - V_{\parallel}) \leq 8/3$ the energy has a unique minimum at $\langle P_2 \rangle = 0$.
- (ii) When $8/3 \leq C(V_{\perp} - V_{\parallel}) \leq 2.7725 \dots$ the free energy has two minima with $\langle P_2 \rangle = 0$ corresponding to the absolute minimum.
- (iii) When $2.7725 \dots \leq C(V_{\perp} - V_{\parallel}) \leq 3$ the free energy has two minima with $\langle P_2 \rangle \neq 0$ corresponding to the absolute minimum.

The system therefore undergoes a phase transition in the neighborhood of the critical concentration where $C(V_{\perp} - V_{\parallel}) = 2.7725 \dots$. In a recent paper Doi (1981), after generalizing the diffusion equation to include the concentration dependence of the diffusion constant and the effect of intermolecular interaction potential arrived at similar results. In his paper the corresponding values of the parameter U (which is defined to be proportional to concentration C) are $8/3$, 2.7 and 3 .

The presence of flow gradient changes the above picture. Plots of free energy vs $\langle P_2 \rangle$ for $(\zeta\gamma/KT) = 0.05$ are shown in figure 6. Note that there is now but one minimum of free energy at each concentration and the occurrence of phase transition is therefore out of question.

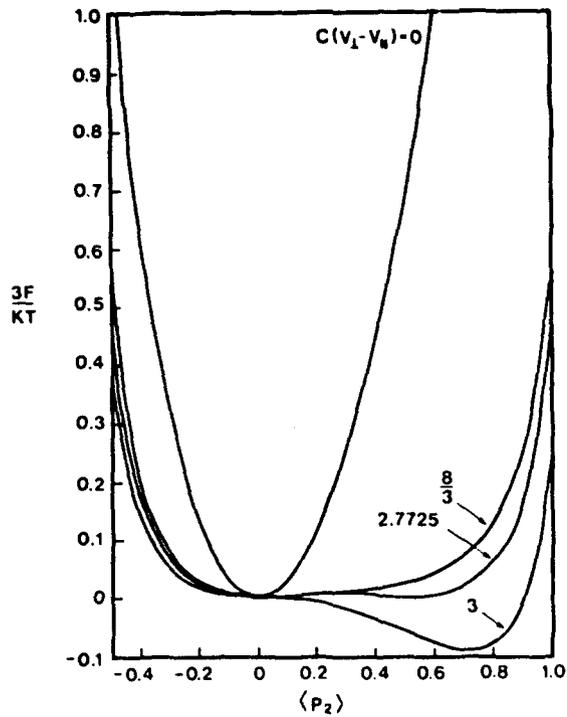


Figure 5. Onsager's free energy vs order parameter in the Zwanzig model. Curves for several concentrations are shown. The macromolecular solution in this case is not flowing.

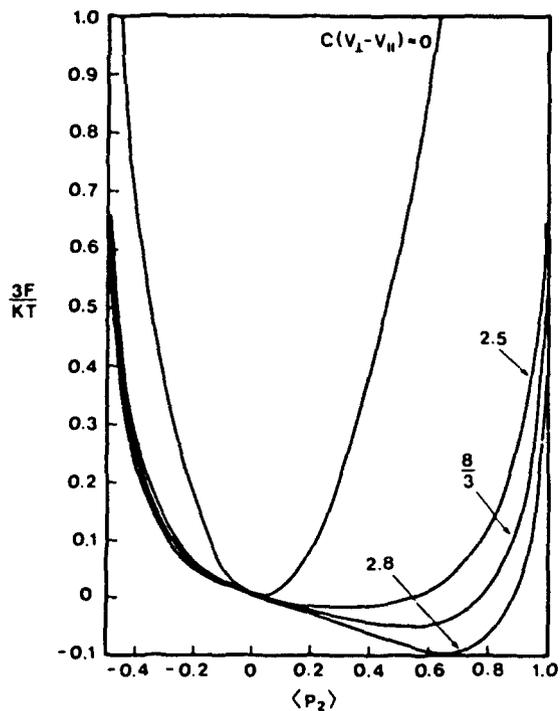


Figure 6. Onsager's free energy vs order parameter in the Zwanzig model. Curves for several concentrations are shown. The macromolecular solution in this case is undergoing flow with $(\zeta/KT) = 0.05$.

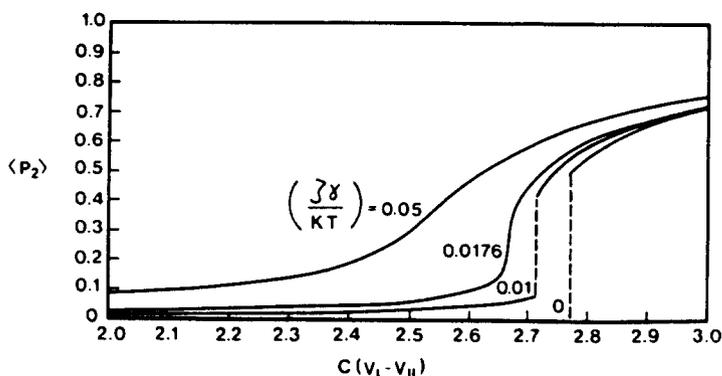


Figure 7. Order parameter vs concentration at different flow gradients (Zwanzig model). If the flow is not too weak, the phase transition disappears.

Figure 7 shows plots of order parameter vs concentration for several values of the flow gradient. It is not difficult to show that the value of $(\zeta\gamma/KT)$ above which the transition disappears is $(2/3)[\ln 2 - (2/3)] = 0.0176$ The curve for this limiting value of $(\zeta\gamma/KT)$ is also shown in Figure 7.

5. CONCLUDING REMARKS

We have studied the behavior of rodlike macromolecules in solution in the presence of a uniaxial extensional flow field. Application of both the Maier-Saupe mean field theory and the theory of Onsager to the problem indicates that the nematic-isotropic phase transition disappears as the flow gradient reaches beyond a certain critical value. This is similar to the results of an earlier study in which Flory's methods had been applied. These results which are mere predictions at this stage now await experimental verification.

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