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# Effects of elongational flow on the isotropic-nematic phase transition in freely-jointed rod systems

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## Summary

The effects of polymer chain flexibility and elongational flow field on the isotropic–nematic phase transition are studied by applying a freely–jointed rods model to the Onsager theory. The biphasic region becomes wider and the difference of order parameters between the coexisting phases becomes larger as the flexibility increases. Also, the onset concentration of highly ordered nematic phase becomes lower, the biphasic region narrower and a difference of the order parameters between the coexisting phases smaller as the stretching rate increases. It is shown that there exists a critical point at a sufficiently high stretching rate, which means the existence of a stable monophase above the critical point. We emphasize that there exists not only a unstable biphasic state but also a stable biphasic state in a weakly stretching rate. Thus the order parameter has double values in this stable biphasic region.

## Introduction

It has been known that the rod–like molecules form anisotropic or liquid crystalline phases (mesophase) in a solution when the concentration of these molecules becomes sufficiently high and simultaneously they orient toward a certain direction. The simplest type of the anisotropic phases is a "nematic" in which the molecules have some order in a certain direction **n** called a director. The mesophase is characterized by long–range orientational and short–range translational order.

There have been several studies(1–4) to describe the nematic phase in terms of rigid–rod models. The nematic phase in the absence of external fields was first considered by Onsager.(1) Flory et al.(2–4) also described in detail the phase equilibria for rod–like and for semi–rigid polymers.

On the other hand, the isotropic–nematic phase transition in a polymer solution in an elongational flow field was first analyzed theoretically by Marrucci et al.(5,6) Molecular alignment in the flow field was considered to be an additional contribution to the Gibbs free energy and was superposed on the equilibrium expression of the Flory theory(2). Stable anisotropic regions was then obtained for the various stretching rates, solute concentrations and the axial ratios of the rods. Bahar and Erman(7) extended the treatment of Marrucci and Ciferri(5) by applying the exact lattice treatment(4) to the equilibrium free energy, which led to markedly different results when compared with the treatment of Marrucci and Ciferri. Thirumalai(8) showed the existence of the critical stretching rate above which only the ordered state was stable even in an infinitely dilute solution. He used the mean field variational method adopted by Onsager to predict the ordering phenomena qualitatively. Khokhlov and Semenov(9) considered the influence of external fields of the dipole and quadrupole types on the liquid crystalline ordering in solutions of rigid rods, freely–jointed rods and persistent semi–rigid macromolecules. Lee(10) described the phase equilibrium of two different nematic phases in a solution under an elongational flow field. See, Doi and Larson(11) studied the stability of steady state solutions to Doi's kinetic equation for rigid rod–like polymers in an arbitrary flow field.

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Our study develops a model for the solutions of freely–jointed rigid rodlike molecules subjected to an elongational flow field and describe the phase behaviors by using an accurate iterative method(12).

## Theoretical Consideration

### (a) Modified Onsager Theory for Freely–jointed Rods Model

Consider a solution of M semi–rigid macromolecules in dialytic equilibrium with the solvent at a temperature T under an uniaxial elongational flow field. One macromolecule is composed of a sequence connection of independently rotating rigid rods of length l and diameter d : axial ratio $x = l/d >> 1$. The number of rods in a macromolecule is N'. The number of rods in a volume V is N=MN', their concentration c=N/V (Figure 1).

The free energy of the solution of freely–jointed rods in the second virial approximation differs from the free energy of the corresponding solution of disconnected rods. That is, in the solution of disconnected rods each rod has the freedom of an independent translational motion while in the case under consideration, only the chain as a whole (but not each rod) can move independently. Hence the contribution of the translational entropy to the free energy is equal to TMln(M/V). For long chains this is much less than the corresponding contribution in the case of solution of disconnected rods TNln(N/V).

Following Onsager theory(1) the interaction of rods is assumed to be due to the pure steric repulsion (no attraction). Then we may write the Helmholtz free energy as follows:

$$\frac{F}{NkT} = \frac{\mu_0(T)}{kT} - 1 + \frac{1}{N'}\ln\frac{c}{N'} + \sigma(f) + bc\rho(f) + \frac{1}{2}Gx^3\alpha(f) \qquad (1)$$

Here $\mu_0(T)$ is the chemical potential of one rod in the solvent at temperature T, $b = (\pi dl^2/4)$. $\sigma$, $\rho$ and $\alpha$ are abbreviations for three functionals of the orientational distribution function f(**u**) for the rods as follows:

$$\sigma(f) = \int \ln[4\pi f(\mathbf{u})]f(\mathbf{u})\, d\mathbf{u} \qquad (2)$$

describing the orientational entropy per rod,

$$\rho(f) = \frac{4}{\pi}\iint K(\mathbf{u},\mathbf{u}')f(\mathbf{u})f(\mathbf{u}')\, d\mathbf{u}d\mathbf{u}' \qquad (3)$$

describing the excluded volume effects of two rods, and

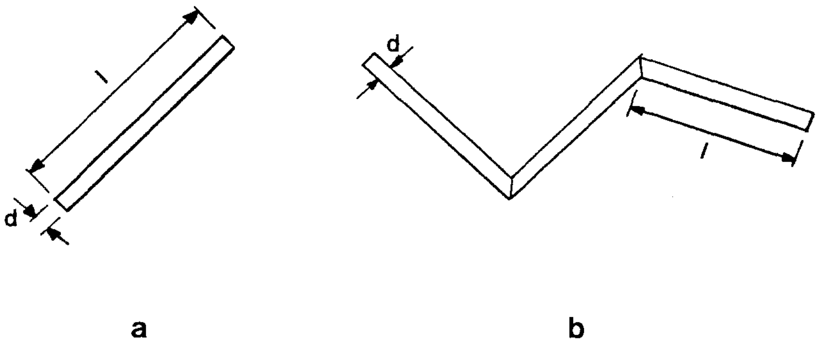

Figure 1. Schematic representation of rod–like molecules:
(a) completely rigid macromolecule
(b) semi–rigid freely–jointed macromolecule.

$$\alpha(f) = \int \sin^2\theta \, f(\mathbf{u}) \, d\mathbf{u} \qquad (4)$$

describing the orientational part of the flow field. The unit vector **u** specifies the direction of a given rod. Also $\theta$ specifies the angle between the rod axis and the flow axis. The kernel $K(\mathbf{u},\mathbf{u}')$ is proportional to the excluded volume related with two rods having orientations **u** and **u'**. In the case of no attraction the kernel can easily be calculated

$$K(\mathbf{u},\mathbf{u}') = |\sin \gamma(\mathbf{u},\mathbf{u}')| \qquad (5)$$

The third term in Eq.(1) is the free energy of the relative motion of the centres of gravity of the macromolecules. The last term is associated with the velocity potential in a steady state elongational flow field(13). G is the dimensionless stretching rate(5):

$$G = \Gamma d^2/(8kT/\zeta) \qquad (6)$$

In Eq.(6), $\Gamma$ is the stretching rate and $kT/\zeta$ is the diffusion coefficient of a macromolecular segment.

By minimizing Eq.(1) with respect to $f(\mathbf{u})$, the nonlinear integral equation is obtained.

$$\ln[4\pi f(\mathbf{u})] = C - \frac{8q}{\pi} \int K(\mathbf{u},\mathbf{u}')f(\mathbf{u}')d\mathbf{u}' - \frac{1}{2} Gx^3\sin^2\theta \qquad (7)$$

where $q = bc$ is a dimensionless concentration and C is a constant determined by the normalization

$$\int f(\mathbf{u}) \, d\mathbf{u} = 1 \qquad (8)$$

We can see that the free energy of Eq.(1) and Eq.(7) coincide with those of Onsager theory as N' and G approach to one and zero, respectively.

(b) Orientational Distribution Function

Without resort to any functional expansions, Eq.(7) can be solved numerically by the iterative method. The form of Eq.(7) suggests that a solution can be obtained by using the following formula

$$f^{m+1}(\theta) = \frac{\exp[-\frac{8q}{\pi}\int K(\mathbf{u},\mathbf{u}')f^{m}(\mathbf{u}')d\mathbf{u}' - \frac{1}{2}Gx^3\sin^2\theta]}{\int \exp[-\frac{8q}{\pi}\int K(\mathbf{u},\mathbf{u}')f^{m}(\mathbf{u}')d\mathbf{u}' - \frac{1}{2}Gx^3\sin^2\theta]d\mathbf{u}} \qquad (9)$$

where m is the iteration number. Lee(10) showed that Eq.(9) was convergent.

The square matrix { K } is introduced to solve Eq.(9) and represents the kernel $K(\mathbf{u},\mathbf{u}')$. Each component has the following form:

$$K(\theta_i,\theta_j') = \int K(\cos^{-1}[\sin\theta_i\sin\theta_j'\cos\varphi' + \cos\theta_i\cos\theta_j'])d\varphi' \qquad (10)$$

where $\varphi'$ is azimuthal angle between $n_i$ and $n_j'$, i and j specify the i–th and j–th element out of n total elements having polar angle $\theta$ and $\theta'$, respectively.

These integrals in Eqs.(9) and (10) are solved by trapezoidal quadrature formula. Lee and Meyer(14) showed that this iterative method gave results independent of n for large n. We have performed numerical iterations in case of $n = 180$ in the system of monodisperse rods.

In the iteration, each step moves in a decreasing direction of the discretized free energy. After sufficiently converging iterations, the solution $f(\theta)$ is independent of the initial form of $f(\theta)$ and represents a well–defined orientational distribution function. However, the solutions depend on the initial form of $f(\theta)$ in the biphasic region. Convergence is assumed when the $f(\theta)$ difference between two successive iterations becomes less than at least $10^{-6}$.

In the case of no flow we find, in general agreement with the other works(11,12), that (i) all initial choices for the orientational distribution function lead to the isotropic distribution function for $q < q_1 = 3.49$; (ii) all initial choices for the orientational distribution function lead to the anisotropic distribution function for

$q > q^* = 3.96$; (iii) for $q_1 \leq q \leq q^*$, a initial choice of $f^O(\theta)$ = const. leads to the isotropic distribution function, but the choice of $f^O(\theta) = a_1 - a_2\theta - a_3\theta^2$, where a's are arbitrary constants, leads to the anisotropic distribution function; (iv) for $q = q_2 = 3.53$, the free energy of the isotropic phase equals to that of the nematic phase.

Doi(15) showed the phase transition as a function of a parameter U by using the generalized diffusion equation. Here U denotes a phenomenological parameter ($=\nu_2 cdl^2$) characterizing the intensity of the interaction potential, where $\nu_2$ is a certain numerical factor. The values of $U_1$, $U_2$ and $U^*$ correspond to those of $q_1$, $q_2$ and $q^*$ for our's results, respectively. The values of U is in quantitative agreement with the values of q in the case of $\nu_2 = 0.6$. Finally we note that the isotropic and nematic phases can stably coexist between $q_1$ and $q^*$, otherwise one of them becomes unstable.

In the nematic phase, a measure of orientation is provided by the order parameter S defined as

$$S = \int f(\theta) \sin\theta \, [\frac{3}{2}\cos^2\theta - \frac{1}{2}] \, d\theta \tag{11}$$

The order parameter varies from zero for a randomly oriented system to unity for complete orientation.

### (c) Isotropic–Nematic Phase Transition

In order to find the transition concentrations of the isotropic ($q_i$) and nematic ($q_a$) phase, we equate the osmotic pressure and chemical potential of each phase :

$$P = -(\frac{\partial F}{\partial V})_{T,N} = kTc(\frac{1}{N'} + q\rho) \tag{12}$$

$$\mu = -(\frac{\partial F}{\partial N})_{T,V} = \mu_0 + kT(\frac{1}{N'} + \frac{1}{N'}\ln\frac{c}{N'} - 1 + \sigma + 2q\rho + \frac{1}{2}Gx^3\alpha) \tag{13}$$

It is convenient to introduce the dimensionless parameters for osmotic pressure and chemical potential. Hereafter, **P** denotes dimensionless osmotic pressure bP/kT and $\boldsymbol{\mu}$ denotes dimensionless chemical potential $(\mu - \mu_0)/kT + 1 + (\ln b)/N' - 1/N'$. Then the coexistence conditions can be expressed as

$$q_i(\frac{1}{N'} + q_i\rho_i) = q_a(\frac{1}{N'} + q_a\rho_a) \tag{14}$$

$$\frac{1}{N'}\ln\frac{q_i}{N'} + \sigma_i + 2q_i\rho_i + \frac{1}{2}Gx^3\alpha_i = \frac{1}{N'}\ln\frac{q_a}{N'} + \sigma_a + 2q_a\rho_a + \frac{1}{2}Gx^3\alpha_a \tag{15}$$

The simultaneous nonlinear equations (14) and (15) are solved by the Newton–Raphson iterative method.

### (d) Effects of Elongational Flow Field

The uniform distribution function $f(\mathbf{u}) = 1/(4\pi)$ does not satisfy Eq.(7) any more for all values of the dimensionless concentration q unless the flow field vanishes. Even in the limit of zero concentration we expect that there exists the orientational order induced by the flow field. In the flow field, for that reason, words such as "isotropic" and "nematic" are replaced with words such as "weakly ordered nematic" and "highly ordered nematic", respectively.

The transition concentration versus the flow parameter $Gx^3$ is plotted for four different numbers N' in Figure 2. There are three phase regions; weakly ordered nematic, biphasic and highly ordered nematic phases.

The freely–jointed rods model includes, of course, the rigid rod–like model as a special case (N'=1) and describes, at least qualitatively, the semi–rigid case (N'= ∞). As the number of rods in a macromolecule N' becomes larger, in other words, a

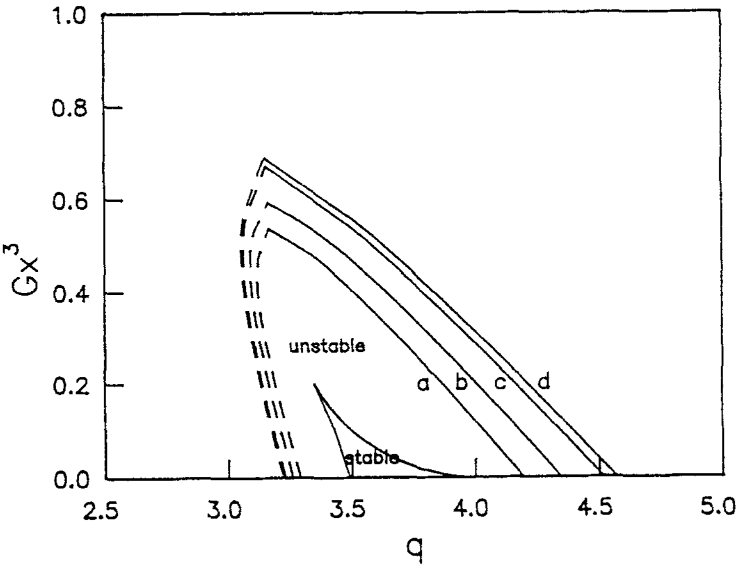

Figure 2. The transition concentrations of the weakly ordered nematic phase and highly ordered nematic phase as a function of the flow parameter (— — —) weakly ordered nematic, (———) highly ordered nematic phase; (a) N'=1 (b) N'=2 (c) N'=10 (d) N'=1000

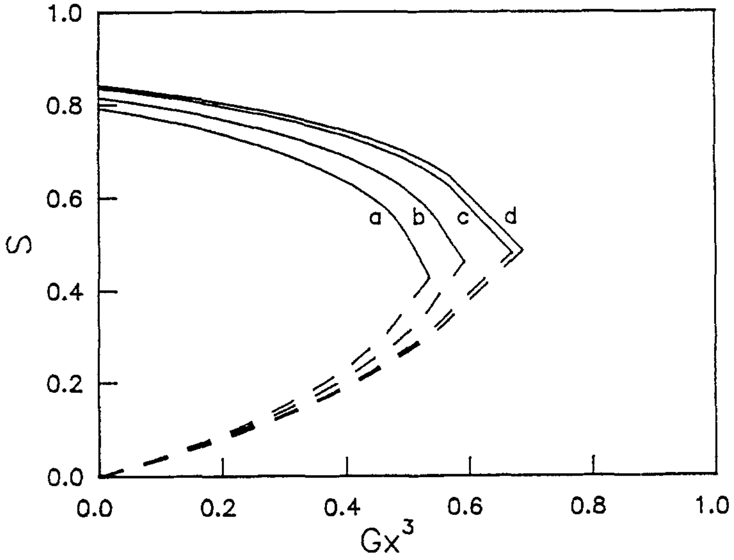

Figure 3. The order parameters of the two nematic phases at the transition as a function of the flow parameter: (— — —) weakly ordered nematic, (———) highly ordered nematic phase; (a) N'=1 (b) N'=2 (c) N'=10 (d) N'=1000

flexibility of the macromolecule increases, $q_i$ becomes smaller and $q_a$ becomes larger. Thus the biphasic region becomes wider. These results agree qualitatively with those of Flory theory(16). However, the calculated transition concentration and biphasic region, based on the Onsager's approximation, are smaller and wider than those of the Flory theory, respectively. As the flow parameter increases, the biphasic region becomes narrower. Thus we can see a critical point ( $q_c = q_i = q_a$ ) at a certain value of flow parameter above which a stable monophase exists. When N' becomes larger, the critical flow parameter becomes larger. However, for N' > 1000 the phase diagram almost does not change.

A general features of these phase diagrams are in qualitative agreement with the other works(5–10). In order to prove the stability of biphasic region as stated previously, the Eq.(9) is solved for two different initial forms of $f(\theta)$. In the case of small $Gx^3$ there exists a stable coexisting state of weakly ordered nematic and highly ordered nematic phases as well as a unstable coexisting state in the biphasic region. Thus, S has double values for one q value in this stable coexisting state as shown in Figure 5(a). These results are in disagreement with those of Lee(10), which show always unstable biphasic regions.

Figure 3 shows the transition order parameters as a function of the flow parameter $Gx^3$ for four different numbers N'. As $Gx^3$ increases, the biphasic region becomes smaller. Thus the order parameter reaches a critical point at which $S_i$ and $S_a$ meets together. For a given $Gx^3$, a difference of the order parameter in the biphasic region becomes larger as N' increases.

Figure 4 shows the order parameters S as a function of the flow parameter $Gx^3$ for four different concentrations q. The lowest curve corresponds to a dilute solution with $q = 2.5$, which shows a very slowly increasing with increasing flow parameter. For the curve for $q = 3.2$, the solution shows a unstable biphasic in the range $0.19 < Gx^3 < 0.52$. Thus S has no double values and increases nonlinearly with $Gx^3$, reaching a relatively high value. We note that in the quiescent state the solution should be isotropic at this concentration. When $q = 3.5$, the solution shows a stable biphasic region for $0 < Gx^3 < 0.11$. The relation of S to $Gx^3$ in this region is shown by the dashed line in Figure 4. Probably overall order parameter may be seen to increase nonlinearly with $Gx^3$ in this region. For $Gx^3 > 0.11$ the solution shows a totally nematic single phase. The change in S with increasing $Gx^3$ is not very high in this region. For $q = 4.5$. the solution is already highly nematic in the quiescent state, which means a very slight change of order parameter with flow parameter.

Figure 5 shows the order parameters S as a function of the dimensionless concentration q for four different flow parameters $Gx^3$. Strong dependence of S on q is observed for all values of $Gx^3$. When $Gx^3 = 0.1$, the solution shows a stable biphasic region for $3.43 < q < 3.50$. Thus S has double values.

## Conclusions

This paper generalizes the Onsager theory by introducing an external flow field and a flexibility of macromolecules to the solution system of rod–like molecules. The phase transition is affected largely by the axial ratio x of the rod but very little by the number of rods in a molecule. Application of the freely–jointed rods model to real chain molecules should be undertaken with caution.(16) For example block copolymers in which one of the blocks is a rigid chain represent a further class of substances having the potentiality for formation of a nematic phase. It is obvious that the nematic ordering induced by the flow field, at a critical value of stretching rate, is

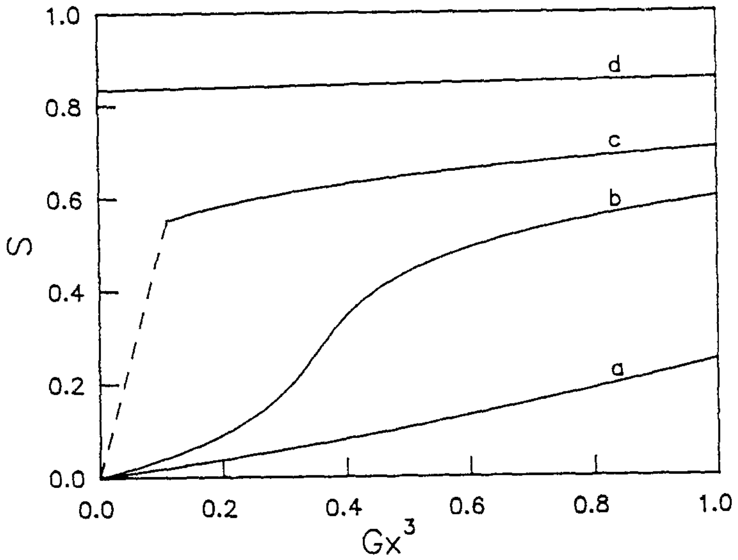

Figure 4. The order parameters as a function of the flow parameter. The dashed line indicates the order parameters in the stable biphasic region:
(a) q = 2.5 (b) q = 3.2 (c) q = 3.5 (d) q = 4.5

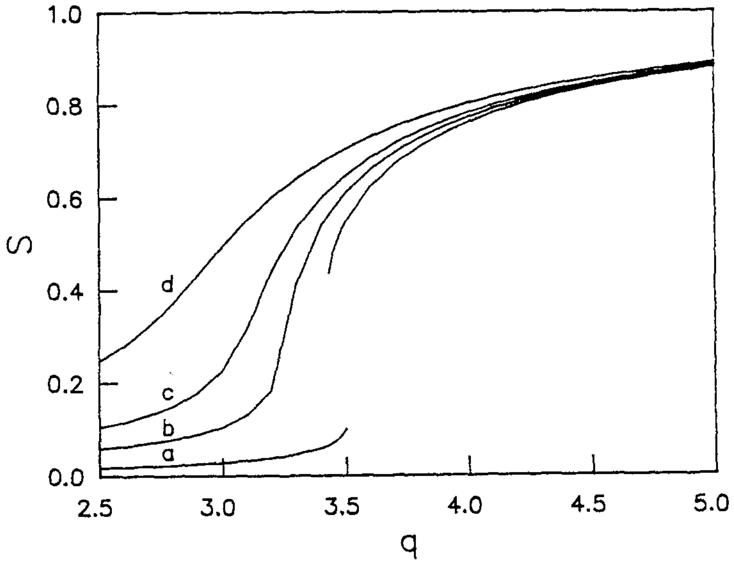

Figure 5. The order parameters as a function of the concentration q.
(a) $Gx^3$=0.1 (b) $Gx^3$=0.3 (c) $Gx^3$=0.5 (d) $Gx^3$=1.0

always accompanied by a phase transition to a highly ordered nematic phase. And it should be emphasized that there exists not only a unstable coexisting phases but also a stable coexisting phases in a weakly stretching rate.

Finally the effect of an elongational flow field on the rod–like systems is more pronounced when the system is close to or in the biphasic state.

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