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Nematic Transition in Solutions of Semiflexible Chains: Influence of an Annealed Size Distribution

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ABSTRACT: The isotropic to nematic transition in solutions of linearly associating semiflexible polymers is studied at the level of the second virial approximation. It is found that, provided the polymers (or aggregates of polymers) are sufficiently long compared to their persistence length, the end-to-end association does not appreciably influence the transition. Strong coupling between the self-assembly and the nematic ordering has, however, to be expected when the polymers are very stiff and the tendency for aggregation is (in the isotropic phase) relatively weak.

A theoretical analysis of the influence of polydispersity on the isotropic to nematic transition in systems of stiff polymers, lyotropic and thermotropic, is far from trivial because of the number of degrees of freedom that are in principle involved. This is particularly true for systems with a quenched size distribution, where each species of the distribution adds to the complexity of the description of the problem. Also, the maximum number of possible coexisting phases increases linearly with the number of components (Gibbs' phase rule), and even when focusing on the isotropic to nematic transition alone, one should expect equilibria involving more than one type of nematic phase. This has indeed been predicted theoretically[1-3] and is confirmed experimentally[4,5] for bidisperse solutions of rodlike macromolecules, where an isotropic phase can coexist with two different nematic phases. These and other studies[6,7] further indicate that polydispersity effects, on the one hand, tend to widen the phase gap in a two-phase equilibrium and, on the other hand, induce a fractionation of molecular weights. (Higher molecular weights favor the nematic phase.) A similar fractionation has also been predicted to occur in melts of polydisperse nematic liquid crystalline polymers.[8] What (according to the theory) is a unique transition temperature for monodisperse polymers[9] becomes a finite temperature gap, the width of which depends on the degree of polydispersity. Within the gap, two phases coexist.

When the size polydispersity is not quenched but annealed, the situation is simplified considerably. The reason is that the size distribution is then an equilibrium quantity and the molecular weight of a species is not an independent variable. As was recently shown for the case of semiflexible wormlike micelles,[10] the statistical thermodynamics of the transition for this kind of polydisperse system is (within the same second virial treatment) no more complicated than for the analogous, but monodisperse, solutions of wormlike polymers. The predicted increase in average size of the self-assembling particles in the nematic phase is now not a proper fractionation process but results from an ordering-induced growth. An example pertaining to thermotropic systems is given by the work of Bladon *et al.*,[11] who discussed the influence of transesterification reactions on the transition of nematic liquid crystalline polymers (producing a different type of annealed size polydispersity because the number of chains is conserved). Here, as for the equivalent quenched case, a finite transition temperature gap was found.

In this paper we describe a second virial theory for the isotropic to nematic transition in solutions of wormlike chains that associate linearly through some mechanism we do not specify in detail. In practice end-to-end association may occur due to the presence of functional end groups. There are, e.g., strong indications that the (equilibrium) aggregates formed by poly(butyl glutamate) in certain solvents are of the end-to-end type,[12] possibly involving hydrogen bonds.[13,14] Our aim is to investigate whether, and if so to what extent, aggregation couples to the transition. As we will see, for *very long* semiflexible polymers the coupling is weak: the self-assembly only responds to the transition but does not seem to influence it appreciably. This is consistent with the theory presented by van der Schoot and Cates in ref 10 for wormlike micellar solutions. The present work differs from that of ref 10 in that here we allow for both weak and strong aggregation, whereas the theory of ref 10 is only valid in the strong growth limit. In the strong growth regime the average aggregation number greatly exceeds the minimum aggregation number. It turns out, however, that coupling between growth ordering is strongest for stiff chains in the regime where aggregation is (in the isotropic phase at least) only moderate.

We model the (unassociated) polymers as semiflexible cylinders of length l, width d, and persistence length P. The polymers are assumed to interact via a hard-core excluded volume. When $l \gg d$ and $P \gg d$, a second virial approximation of the free energy gives an adequate description (see, e.g., reviews in refs 15 and 16). We (for reasons of simplicity) take the formal limit $P/d \to \infty$, $l/d \to \infty$, while keeping $x \equiv l/P > 0$ constant. It implies that at the transition the volume fraction polymer ϕ will tend to zero, $\phi \propto d/P \to 0$. Anticipating this, we define a scaled volume fraction $c \equiv \phi P/d$ that remains finite and roughly of order unity at the transition (in fact, $c \approx 10$ at the transition). Let $c(n)$ denote the scaled volume fraction of n-mers, i.e., of linear aggregates consisting of n chains ($n = 1, 2, 3, \ldots$). These aggregates are viewed again as semiflexible cylinders, of the same diameter and persistence length as the single chains but of variable length nl. We suppress the possibility of ring closures. The dimensionless free energy density f can now be written as

$$f = \sum_{n=1}^{\infty} c(n)\, n^{-1}[\ln(c(n)\, n^{-1}) - 1 + E + \sigma(n) + \sum_{m=1}^{\infty} c(m)\, m^{-1} B(n,m)] \quad (1)$$

Here we have set the thermal energy equal to unity ($k_B T$

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$\equiv 1$) and multiplied a free energy per unit volume by the volume of a single chain $\vartheta \equiv \pi l d^2/4$ and by the ratio P/d. Equation 1 consists of an ideal mixing entropy, a free energy penalty E for having free ends on a chain, a term $\sigma(n)$ signifying the loss of orientational entropy of a chain when going from the isotropic to the nematic state, and an interaction term involving the second virial coefficients $B(n,m)$ of two species of size n and m. By definition $\sigma(n) = 0$ in the isotropic phase.

Provided the aggregates are sufficiently long in the nematic phase (on average much larger than the relevant length scale in the nematic, the so-called deflection length $\lambda \ll P$), we can always write $\sigma(n)$ as the sum of a term independent of the size of the chain and a term linear in its size,[15,17]

$$\sigma(n) = \sigma_0 + n\sigma_1 \qquad (2)$$

where σ_0 and $\sigma_1 \equiv x = l/P$ are both a function of the degree of orientational order and independent of n. These two quantities can be attributed to contributions from the ends and midsections of the aggregates, respectively. It is at this point not necessary to specify σ_0 and σ_1.[18] We will do that later on and give an estimate of the range of validity of eq 2.

The second virial coefficients $B(n,m)$, in eq 1 made dimensionless through division by $\vartheta P/d = \pi l d P/4$, can be approximated by[15,17,19]

$$B(n,m) = nmx\rho \qquad (3)$$

End effects in the interaction do not contribute, because we operate in the limit $l/d \to \infty$, $P/d \to \infty$. The factor ρ appearing in eq 3 expresses the reduced excluded-volume interaction in the nematic phase: $\rho = 1$ in the isotropic and $\rho < 1$ in the nematic phase. It is not yet necessary to describe this quantity explicitly, and we leave it, for the time being, as an unknown function of the degree of order.

The equilibrium size distribution minimizes the free energy (1) given the constraint of conservation of mass, $\sum c(n) = c$, yielding (for both the isotropic *and* the nematic phase)

$$c(n) = 4cn(1 - N^{-1})^n((2N - 1)^2 - 1)^{-1} \qquad (4)$$

where $N = c/\sum c(n)\, n^{-1}$ is the average aggregation number, obeying[20]

$$N = \frac{1}{2} + \frac{1}{2}[1 + 4cG^2 \exp(\sigma_0)]^{1/2} \qquad (5)$$

Here $G^2 \equiv (d/P) \exp(E)$ is the "growth parameter",[21] an important factor determining the average size of the chains: when $G \ll 1$, $N \sim 1 + cG^2 \exp(\sigma_0)$, and when $G \gg 1$, $N \sim c^{1/2} G \exp(^1/_2\sigma_0)$. We immediately see that (a) self-assembly is enhanced in the nematic phase because there $\sigma_0 > 0$,[18] whereas $\sigma_0 \equiv 0$ in the isotropic phase, (b) only end effects in the orientational entropy influence growth, (c) $c(n)$ becomes a step function if $N \to 1$, with $c(1) = c$ and $c(n{>}1) = 0$, and (d) for $N \gg 1$ eq 4 asymptotes to an exponential distribution: $c(n)/n \sim cN^{-2} \exp(-n/N)$ (a well-known result in the strong growth regime[22]).

Equilibrium between a nematic and an isotropic phase implies equality of the chemical potentials of the chains, $\mu = \partial f/\partial c|_{V,T}$, and equality of the osmotic pressures, $\Pi\vartheta(P/d) = \mu c - f$. Inserting eqs 4 and 5 into the free energy gives

$$f = \sigma_1 c + x\rho c^2 + c \ln(1 - N^{-1}) - cN^{-1} \qquad (6)$$

Equating the chemical potential in the coexisting phases thus yields (the subscripts i and n referring to the isotropic and nematic phase),

$$\ln(1 - N_\mathrm{i}^{-1}) + 2xc_\mathrm{i} = \ln(1 - N_\mathrm{n}^{-1}) + 2xc_\mathrm{n}\rho + \sigma_1 \qquad (7)$$

while a balancing of osmotic pressures leads to

$$c_\mathrm{i}N_\mathrm{i}^{-1} + xc_\mathrm{i}^{\,2} = c_\mathrm{n}N_\mathrm{n}^{-1} + xc_\mathrm{m}^{\,2}\rho \qquad (8)$$

In the limit $G \ll 1$ these equations agree with those derived for monodisperse wormlike polymers,[15–17] while for $G \gg 1$ they reduce to the equations derived in ref 10 for long wormlike micelles.[23] It is evident that the two asymptotic limits $x = l/P \to \infty$ and $G \to \infty$ yield identical results for the coexisting concentrations c_i and c_n. This means that (a) growth couples only passively to the transition when the polymers are very long and (b) short chain fragments behave in the strong growth limit very much like long polymers. Corrections due to finite size and/or the influence of the self-assembly of the chains must be small when x or G are much larger than unity and will depend explicitly on both x and G. Deviations do become significant when x and G are not so large, i.e., when the chains are stiff and growth is in principle not strong. To show this, we first have to specify σ_0, σ_1, and ρ.

Let the chain-averaged distribution function of the angle between the tangent of a chain and the nematic director be approximated by a Gaussian of mean-square angle $2\alpha^{-1}$, where we assume that $\alpha \gg 1$. The following relations then hold to leading order in α: $\sigma_0 \sim \ln \alpha/4$, $\sigma_1 \sim l/4\lambda$, $\lambda \sim P/\alpha$, and $\rho \sim 4/(\pi\alpha)^{1/2}$.[15] The concentration dependence of α can now be obtained by inserting these expressions into the free energy (6) and subsequently minimizing the result with respect to α, yielding

$$\frac{8c_\mathrm{n}}{\pi^{1/2}\alpha^{3/2}} = 1 + O\left(\frac{\lambda}{L_\mathrm{n}}\right) \qquad (9)$$

where $L_\mathrm{n} = N_\mathrm{n} l$ is the average length of the chains in the nematic. Because we assumed from the outset that $L_\mathrm{n} \gg \lambda = P/\alpha$ for eq 2 to hold, we approximate eq 9 by $\alpha^{3/2} = 8c_\mathrm{n}/\pi^{1/2}$. This should be a reasonable approximation whenever, say, $L_\mathrm{n}/\lambda > 15$, and is consistent with the level of accuracy provided by the Gaussian approximation.[15]

For $x = l/P \to \infty$ or $G \to \infty$, eqs 7 and 8 simplify to $2c_\mathrm{i} = 5\pi^{-1/3}c_\mathrm{n}^{2/3}$ and $c_\mathrm{i}^2 = 2\pi^{-1/3}c_\mathrm{n}^{5/3}$, respectively. The solution to these equations reads $c_\mathrm{n} = (5/2)^6/8\pi \simeq 9.71$ and $c_\mathrm{i} = 4c_\mathrm{n}/5 \simeq 7.77$, so that $\alpha \simeq 12.4$ and the usual orientational order parameter[16] becomes $\eta \simeq 1 - 3\alpha^{-1} \simeq 0.76$. When $G \to \infty$, we find $N_\mathrm{n}/N_\mathrm{i} \simeq 1.97$ at the transition (*cf.* ref 10).

Outside the limit of infinitely long polymers (or aggregates of polymers) eqs 7 and 8 are not so straightforward to solve analytically. Hence, we solved these equations numerically instead, using a standard Newton–Raphson iteration scheme. Results are presented in Figures 1 and 2, where we give the phase diagram and the ratio of the average aggregation numbers in the coexisting phases for various values of x. The figures clearly indicate that, for chains longer than roughly one persistence length (i.e., $x > 1$), self-assembly is essentially enslaved by the nematic ordering. End effects and effects stemming from the self-assembly influence the transition to the same order of magnitude. On the other hand, when the polymers are more or less rodlike ($x \ll 1$), growth and ordering do couple strongly, leading to an enhanced growth in the nematic phase, particularly when growth in the isotropic phase is only moderate, that is, when $G \approx 1$. A maximum appears in the $N_\mathrm{n}/N_\mathrm{i}$ *versus* G curve around this value (note that $N_\mathrm{n}/N_\mathrm{i} \to 1$ when $G \to 0$). Our results further suggest that

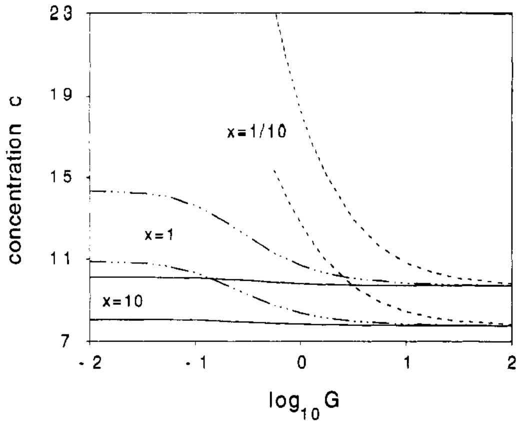

Figure 1. Concentrations in coexisting isotropic and nematic phases of linearly associating semiflexible polymers as a function of the growth parameter G defined in the text. Curves are shown for three different values of the "chain stiffness" x, the ratio of the length of the "monomeric" chains, and their persistence length. The bottom curve of each pair pertains to the isotropic phase and the top curve to the nematic phase. Not shown (for clarity) are curves for which $x = ^1/_2$ and $x = ^1/_5$. (These are very similar to the $x = ^1/_{10}$ coexistence curves, in that they bend upward very steeply with decreasing values of the growth parameter.)

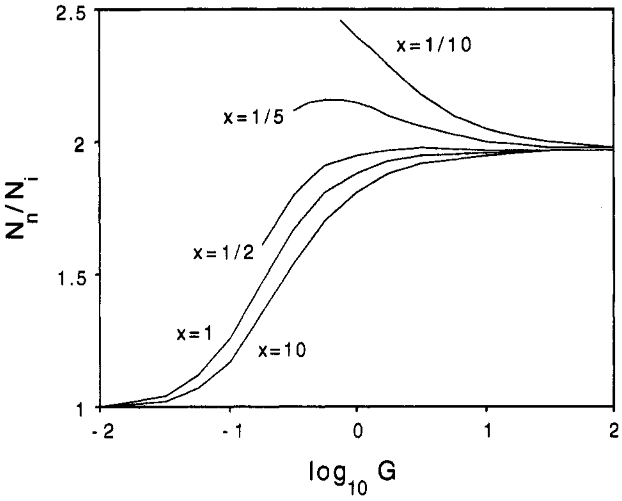

Figure 2. Average length ratios in the coexisting isotropic and nematic phases as a function of the growth parameter G. Curves are shown for varying values of x. As in Figure 1, only results are shown for which $L_n/\lambda > 15$ (see the text).

growth may become unbounded when $x \to 0$, leading to an extremely ordered high density nematic. This would be in accord with the theory of ref 24, describing the isotropic–nematic transition in solutions of perfectly rodlike micelles, where the predicted runaway instability was interpreted in terms of a neglect of micellar flexibility (see also refs 10 and 25).

In conclusion, when semiflexible polymers (or aggregates of polymers) are sufficiently long, end association does not appreciably influence the transition from an isotropic to a nematic solution, even though the aggregates may be much longer in the nematic than in the isotropic phase. Coupling between self-assembly and the transition becomes more prominent the stiffer the chains are.

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