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ABSTRACT: The statistical physics of lyotropic polymer liquid crystals is reviewed and extended, an analysis being given of the effect of the third virial coefficient, charge, semiflexibility, bidispersity, and polydispersity. The isotropic–nematic phase transition is discussed for long rods along the lines of the virial expansion, and the influence of bidispersity and polydispersity is considered. For polyelectrolytes the effects of twist and an increased effective diameter on liquid crystal formation are treated. This is extended to bidisperse and semiflexible polyelectrolytes. The configurational entropy of nematic semiflexible polymers is calculated by different methods and is shown to differ markedly from that of rigid rods. The effect of semiflexibility on the phase transition is analyzed for both mono- and bidisperse systems, the theory agreeing well with data on slender polymer chains like schizophyllan and poly(γ-benzyl L-glutamate).

I. Introduction

A perusal of the literature shows that the field of lyotropic polymer liquid crystals has developed unsteadily. In a review of more than a decade ago Straley[1] lamented that one could not empirically verify Onsager's theory[2] of the isotropic–nematic transition owing to the paucity of experiments performed up to that time. Since then a huge number of experiments have been carried out, but concomitantly the theoretical viewpoint has also shifted. We now realize that the behavior of real systems of semiflexible polymers can significantly differ from that of a solution of rods that are ideally chosen to be very slender and hard. It is imperative to account for these differences. Here we review and extend theoretical developments since Straley's survey, concentrating on the virial expansion. A comparison with experimental results is also given.

The waxing interest in lyotropic polymer nematics is connected with the increasing importance of several other related fields: the manufacture of extremely strong fibers; characterization of the stiffness and other parameters of biopolymers; lyotropic systems in general; elastically stiff systems like membranes and micelles; and so forth. Many workers in the fields of simple liquid crystals and flexible polymers have been turning to more complicated systems like semiflexible polymers because both fields have reached temporary plateaus in their development. The number of recent reviews[3-16] attests to the present-day relevance of polymer liquid crystals in general. Still, several topics

have been reviewed only summarily, so the author hopes the discussion of these topics will complement existing surveys.

II. Onsager Theory for Long Rods

In this section we discuss the isotropic–nematic phase transition for a semidilute solution of slender, perfectly rigid, rodlike polymers in the second virial approximation. We formulate the Helmholtz free energy ΔF, postulate isotropic and nematic phases, minimize ΔF to get the particle distribution functions, derive coexistence equations for the polymer chemical potential and osmotic pressure, and solve the resulting coupled equations, discarding unstable solutions.

In setting up this program for our solution of N rodlike macromolecules in a volume V, we can view the system as a gas of N rods provided we use the potential of mean force between the polymers. This potential w will be a function of the vector distance r_{nm} between two test rods n and m and also of their orientations a_n and a_m, these being specified with respect to the director n when the phase is nematic. If the solution or gas is not too concentrated, it is plausible to start with a virial expansion, which must be amended for systems with orientational degrees of freedom. This is conveniently done by introducing the single-rod orientational distribution function $f(a)$. The extension of the usual virial or cluster expansion for the Helmholtz free energy ΔF is as follows:[2]

$$\frac{\Delta F}{N k_{\rm B} T} =$$

$$\frac{\mu^{\circ}(T,\mu_0)}{k_{\rm B}T} - 1 + \ln c' - \Delta S_{\rm or} + B_2 c' + \tfrac{1}{2}B_3 c'^2 + ... \quad (\text{II}.1)$$

$$\int f(\mathbf{a}) \, d\Omega = 1 \quad (\text{II}.2)$$

with orientational entropy

$$\Delta S_{\rm or} = - \int f(\mathbf{a}) \ln \left[4\pi f(\mathbf{a}) \right] \, d\Omega \equiv -\sigma \quad (\text{II}.3)$$

number density $c' = N/V$, and temperature T. The virial coefficients B_i are given in terms of the cluster integrals $\beta_i(\mathbf{a},\mathbf{a}',...)$ pertaining to fixed particle orientations. The first two coefficients are

$$B_2 = -\tfrac{1}{2} \int \int \beta_1(\mathbf{a},\mathbf{a}')f(\mathbf{a})f(\mathbf{a}') \, d\Omega \, d\Omega' \quad (\text{II}.4)$$

$$B_3 = -\tfrac{2}{3} \int \int \int \beta_2(\mathbf{a},\mathbf{a}',\mathbf{a}'')f(\mathbf{a})f(\mathbf{a}')f(\mathbf{a}'') \, d\Omega \, d\Omega' \, d\Omega'' \quad (\text{II}.5)$$

The irreducible cluster integrals β are in turn related to the potential via the Mayer function $\Phi_{mn} = \exp(-w_{mn}/k_{\rm B}T) - 1$, with $w_{mn} = w(\mathbf{r}_m,\mathbf{r}_n,\mathbf{a}_m,\mathbf{a}_n)$

$$\beta_1 = \frac{1}{V} \int \int \Phi_{mn} \, d\mathbf{r}_m \, d\mathbf{r}_n \quad (\text{II}.6)$$

$$\beta_2 = \frac{1}{2V} \int \int \int \Phi_{mn}\Phi_{no}\Phi_{om} \, d\mathbf{r}_m \, d\mathbf{r}_n \, d\mathbf{r}_o \quad (\text{II}.7)$$

The free energy ΔF is simply a sum of the ideal chemical potential (μ° is the reference state for solvent of chemical potential μ_0), a negative entropy increasing with alignment and a sum of virial terms decreasing upon orientational ordering. Note that we have assumed negligible three-body potentials w_{mno}, an assumption that could be serious for some real systems.

Let us defer discussion of the effect of the third virial coefficient to the next section. For now we focus on the isotropic-to-nematic transition for long, hard rods of diameter D and length L in the second virial approximation. First, the parameters β_1 and B_2 (or b) are very well known[2]

$$b \equiv B_{2,i} = (\pi/4)L^2 D \quad (\text{II}.8)$$

$$\beta_1 = -2L^2 D |\sin \gamma| \quad (\text{II}.9)$$

Here we have used the results for the isotropic average of the sine of the angle $\gamma(\Omega,\Omega')$ between two test rods $\langle \langle |\sin \gamma| \rangle \rangle_i = \pi/4$. At this stage we do not carry terms of order $D^2 L$ (see section III). The quantity b is half the excluded volume between two rods if they were randomly oriented. It is convenient to introduce the dimensionless parameters ρ and c, proportional to the orientational pair excluded volume

$$c = bc' \quad (\text{II}.10)$$

$$\rho = \frac{4}{\pi}\langle\langle|\sin \gamma|\rangle\rangle = \frac{4}{\pi} \int \int |\sin \gamma(\Omega,\Omega')|f(\Omega)f(\Omega') \, d\Omega \, d\Omega' \quad (\text{II}.11)$$

Thus, in the isotropic phase, $\sigma = 0$ and $\rho = 1$ whereas $\sigma > 0$ and $\rho < 1$ in the nematic phase. Finally we can rewrite the free energy in view of eq II.1, II.2, and II.8–11

$$\frac{\Delta F}{N k_{\rm B} T} = \text{constant} + \ln c + \sigma(f) + c\rho(f) \quad (\text{II}.12)$$

Minimizing eq II.12 leads directly to a nonlinear integral equation (see eq III.28) which we discuss later on. Another way of proceeding is to choose a normalized trial function f depending on adjustable parameters $\alpha_1, \alpha_2, ...$ and then

minimize eq II.12 with respect to $\alpha_1, \alpha_2, ...$ For instance, Onsager chose

$$f(\theta) = \left(\frac{\alpha}{4\pi \sinh \alpha} \right) \cosh (\alpha \cos \theta) \quad (\text{II}.13)$$

where θ is the angle between the director and the test rod. Equation II.13 is particularly suitable because it enables us to accommodate the isotropic state ($\alpha = 0$, $f = 1/4\pi$), slightly nematic states ($f(\theta) = $ (constant 1) + (constant 2) $\cos^2 \theta$), and highly ordered states ($\alpha \gg 1$, $f(\theta) \sim$ Gaussian). Thus, the behavior of f makes good physical sense for all α and θ.

However, the mathematics of dealing with eq II.13 is still involved. Thus, for illustrative purposes but also because we will have very good reason to use it later on, let us for the moment simply choose the crude Gaussian limit of eq II.13 as our trial function for the nematic phase

$$f(\theta) = \left(\frac{\alpha}{4\pi} \right) e^{-\alpha\theta^2/2} \quad (0 \le \theta \le \tfrac{1}{2}\pi)$$

$$= \left(\frac{\alpha}{4\pi} \right) e^{-\alpha(\pi-\theta)^2/2} \quad (\tfrac{1}{2}\pi \le \theta \le \pi) \quad (\text{II}.14)$$

Note that the normalization is not exact but should include exponentially small terms of $\mathcal{O}(\exp(-\alpha))$ (α can in fact be large in practice). Equation II.14 implies

$$\langle \theta^2 \rangle = 2/\alpha \quad (\alpha \gg 1) \quad (\text{II}.15)$$

Hence, typically the relevant angles θ, θ', and γ in the kernal of eq II.11 are all small so that using the trigonometrical rule $\cos \gamma = \cos \theta \cos \theta' + \sin \theta \sin \theta' \cos \varphi$, we have

$$\gamma^2 \simeq \theta^2 + \theta'^2 - 2\theta\theta' \cos \varphi \quad (\text{II}.16)$$

with θ and θ' the angles between the respective rods and director, and φ the angle between the projections of the rods onto a plane perpendicular to the director. Therefore, we know at once that $|\sin \gamma|$ and thus $\rho_a(\alpha) = \mathcal{O}(\alpha^{-1/2})$. The numerical coefficient can also be calculated. Equations II.11, II.14, and II.16 yield

$$\rho_a(\alpha) \sim 4(\pi\alpha)^{-1/2} \quad (\text{II}.17)$$

The calculation of σ (eq II.3) is straightforward

$$\sigma_a(\alpha) \sim \ln \alpha - 1 \quad (\text{II}.18)$$

In eq II.17 and II.18 the index a refers to the anisotropic (nematic) phase. The total free energy becomes

$$\frac{\Delta F}{N k_{\rm B} T} \sim \text{constant} + \ln \alpha + 4\pi^{-1/2}c_a\alpha^{-1/2} \quad (\text{II}.19)$$

This expression exhibits the balance of orientational confinement ($\ln \alpha$ or $-\ln \langle \sigma^2 \rangle$) vs. excluded volume ($c_a\alpha^{-1/2}$ or $bc_a'\langle\theta^2\rangle^{1/2}$). Minimization of eq II.19 leads to

$$\alpha^{1/2} = 2\pi^{-1/2}c_a \quad (\text{II}.20)$$

Accordingly, the characteristic deviation of a rod from the director is inversely proportional to the number density.

In view of eq II.20 we now know the free energy (eq II.12) as a function of the number density in the anisotropic phase as well as the isotropic phase. The concentrations in the phases are connected by the coexistence equations. The osmotic pressure Π' is given by

$$\Pi' = -\left(\frac{\partial \Delta F}{\partial V} \right)_{T,\mu_0,N} = k_{\rm B}Tc'(1 + c\rho) \quad (\text{II}.21)$$

The chemical potential μ' of the rodlike macromolecules is

$$\mu' = -\left(\frac{\partial \Delta F}{\partial N}\right)_{T,\mu_0,V} = \mu^\circ + k_B T(\ln c' + \sigma + 2c\rho) \quad \text{(II.22)}$$

In the following the index i refers to the isotropic phase, and a to the nematic one. Coexistence implies $\Pi_i' = \Pi_a'$ and $\mu_i' = \mu_a'$. Moreover, in the isotropic phase we know that $\sigma_i = 0$ and $\rho_i = 1$. Thus, the coexistence equations are simply

$$c_i(1 + c_i) = c_a(1 + c_a\rho_a) \quad \text{(II.23)}$$

$$\ln c_i + 2c_i = \ln c_a + \sigma_a + 2c_a\rho_a \quad \text{(II.24)}$$

There are two sets of solutions to eq II.17–24: $\alpha_0 = 33.40$, $c_{i,0} = 3.45$, and $c_{a,0} = 5.12$; $\alpha_0^* = 0.538$, $c_{i,0}^* = 0.983$, and $c_{a,0}^* = 0.650$. Evidently the latter set is useless because α_0^* is not large. We explicitly give both solutions because they will be needed quite precisely in fact in section IV.

Is the first solution stable? We demand that $\Delta F_a(\alpha_0)$ is a minimum and furthermore that the nematic state is stable compared with the isotropic one: $\Delta F_a(c_a) < \Delta F_i(c_a)$. Both requirements are met. The phase transition is first order although only weakly.[94] Naturally, use of the trial function given by eq II.13 leads to a much more precise theory.[2] We also outline this in some detail and precision because it will function as a zero-order theory for perturbation schemes in later sections. The calculation of σ is easy whereas that of ρ is not as can be discerned from the appendix to ref 2.

$$\sigma_a(\alpha) = \ln \alpha - 1 + \pi e^{-\alpha} + \mathcal{O}(e^{-2\alpha}) \quad \text{(II.25)}$$

$$\rho_a(\alpha) = \frac{2I_2(2\alpha)}{(\sinh \alpha)^2} \sim 4(\pi\alpha)^{-1/2}\left[1 - \frac{15}{16\alpha} + \frac{105}{512\alpha^2} + \frac{315}{8192\alpha^3} + ...\right] \quad (\alpha \gg 1) \quad \text{(II.26)}$$

where I_2 is a Bessel function. The minimization of eq II.12 yields

$$\sigma_a'(\alpha) + c_a\rho_a'(\alpha) = 0 \quad \text{(II.27)}$$

The numerical solution of eq II.23–27 gives[2] $c_i = 3.3399$, $c_a = 4.4858$, $c_a/c_i = 1.3431$, $\alpha = 18.584$, $\rho_a = 0.49740$, $\sigma_a = 1.9223$ as the only stable nematic solution.

As we have already emphasized, we have given the above approximate analyses in some detail because they will be useful in later extensions. Of course, a full numerical analysis of the minimization problem is standard nowadays, although more complex problems can easily pose formidable numerical problems. Direct minimization of eq II.12 yields

$$\ln [4\pi f(\Omega)] = C - \left(\frac{8c}{\pi}\right)\int |\sin \gamma(\Omega,\Omega')| f(\Omega') \, d\Omega' \quad \text{(II.28)}$$

with C a normalization constant determined by eq II.2. Kayser and Raveché[17] have given an elegant bifurcation analysis[18] of eq II.28. They took advantage of the properties of the symmetric kernel $|\sin \gamma|$. Branching of the solution exists when a suitable linear equation associated with eq II.28 (taking account of the normalization eq II.2) has nontrivial solutions. Writing $4\pi f(\Omega) = 1 + h(\Omega)$, one finds[17] that rather plausibly $h \sim P_2(\cos \theta)$ and the bifurcation number density $c^* = 4$. Hence the existence of the nematic phase is rigorously proven at sufficiently high concentrations. It will take us too far afield to discuss in detail the numerical analysis of the global solutions. Kayser and Raveché[17] expanded h or f in Legendre polynomials, the initial coefficients in the expansion being conveniently chosen, and h was inserted in the right-hand side of eq II.28 so that the left-hand side gave a new es-

timate of the coefficients. This process was repeated until convergence was obtained. Another fast procedure is due to Lekkerkerker et al.:[20] expand the kernel in Legendre polynomials, derive expressions for $f(\theta)$, and find the coefficients by inserting f in eq II.2 and II.28. The two sets all but coincide:

$$c_i = 3.2904, \qquad c_a = 4.1910$$

$$\sigma_a = 1.6020, \qquad \rho_a = 0.5651$$

$$\text{order parameter } S = \langle P_2(\cos \theta) \rangle = 0.7922$$

A comparison of these values with those obtained via eq II.13 shows that the use of simple trial functions gives a reasonable semiquantitative theory.

III. Effect of the Third Virial Coefficient

Unfortunately, in real life, macromolecules are almost never slender enough for the second virial approximation to hold precisely, and if they are they tend to be semiflexible. Hence an analysis of the influence of the third virial coefficient is warranted because its effect is determined by $\omega = D/L$ or D/P, where P is the persistence length. Once we incorporate B_3 into the free energy we must also take into account end effects in B_2. Both corrections are of the same order of magnitude. We calculate the cluster or virial coefficients by assuming the trial function of eq II.13. First, from ref 2 we have for a general f

$$-\beta_1(\gamma) = 2L^2D|\sin \gamma| + LD^2(\tfrac{1}{2}\pi(1 + |\cos \gamma|) + 2E(\sin \gamma)) + \mathcal{O}(D^3) \quad \text{(III.1)}$$

The first term is eq II.9, E is the complete elliptic integral of the second kind, and we need not retain $\mathcal{O}(D^3)$ terms. Again in ref 2 we can find the isotropic average of β_1

$$2B_{2,i} = -\langle \beta_1 \rangle_i = 2b(1 + \tfrac{1}{2}\omega(\pi + 3)) \quad \text{(III.2)}$$

Here, the inverse axial ratio $\omega = D/L$ is considered to be much smaller than unity. It is straightforward to obtain the nematic average of eq III.1 for large α by expanding $\cos \gamma$ and $E(\sin \gamma)$ in terms of γ and using eq II.13

$$2B_{2,a} = -\langle \beta_1 \rangle_a = 2b\rho_a(\alpha) + 8\omega b(1 - \alpha^{-1}) + \mathcal{O}(\alpha^{-2}) \quad \text{(III.3)}$$

Straley[19] has given an extensive discussion of β_2 and its averages but there are virtually no analytic results useful in the context of this paper. However, his numerical results do come in handy for our own discussion. The isotropic average of β_2 for $\omega \lesssim 0.05$ given in Table 1 of ref 19 can be cast into a form accurate to within a few percent.

$$\tfrac{3}{2}B_{3,i} = -\langle \beta_2 \rangle_i = K_i\omega b^2 \quad \text{(III.4)}$$

Here Straley's C is $-\langle \beta_2 \rangle_i$ and the numerical coefficient K_i should be about 6.16 in order that eq III.4 agrees with his table. This result is not surprising: the volume excluded to a third rod by two others in such a way that all three touch must be proportional to $LD^2 = \omega b$ if the typical angles between them are not small as in the isotropic state. Straley[19] calculated C or $\langle \beta_2 \rangle_a$ for $f(\theta) \sim \exp(-A \sin^2\theta)$. For large A this is close enough to eq II.13 to set $2A \simeq \alpha$. Straley's numerical values in his Table 1 are rather accurately represented by

$$\tfrac{3}{2}B_{3,a} = -\langle \beta_2 \rangle_a = K_a\alpha^{-3/4}\omega^{3/5}b^2 \quad \text{(III.5)}$$

with $K_a = 7.66$. It is hard to understand the ω dependence but the exponents can be connected by scaling arguments which we first explain for the second virial coefficient in the Gaussian approximation. We first set

$$B_{2,a} \simeq L^2D\alpha^u$$

because $B_{2,a} \rightarrow B_{2,i}$ when $\alpha = \mathcal{O}(1)$. If $\langle \gamma^2 \rangle \simeq \omega^2$ we have essentially parallel rods so that $B_{2,a} \simeq D^2 L$. But we also have $\alpha \simeq \omega^{-2}$ from eq II.15, implying that $u = -1/2$. Hence, we regain the main power dependence of eq III.3. The third virial coefficient is much more complicated because there are three angles to reckon with. If we set $B_{3,a} \simeq \alpha^v L^4 D^2 \omega^{3/5}$ we get $v = -0.7$ because $B_{3,a} \simeq L^2 D^4$ when $\alpha \simeq \omega^{-2}$; i.e., all three rods are almost parallel. Hence, v is very close to the numerical exponent in eq III.5.

Clearly the small parameter in the problem at hand is the inverse axial ratio ω. It is natural to set up a perturbation theory with the zero-order theory being that of the previous section and ω (or some function of ω) as the pertubation parameter. We first minimize the free energy of eq II.1 using eq III.3 and III.5

$$\sigma'(\alpha) + c_a \rho_a'(\alpha) + T_1(\alpha) = 0 \qquad \text{(III.6)}$$

with

$$T_1(\alpha) = 4c_a \omega \alpha^{-2} - \tfrac{1}{4} K_a c_a^2 \omega^{3/5} \alpha^{-7/4} \qquad \text{(III.7)}$$

As in the previous section we derive the coexistence equations in scaled units from eq II.1 by calculating the osmotic pressure and chemical potential of the rods in the respective phases

$$c_i = c_i^2 + T_{2,i} = c_a + c_a^2 \rho_a + T_{2,a} \qquad \text{(III.8)}$$

with

$$T_{2,i} = \tfrac{1}{2}(\pi + 3)c_i^2 \omega + \tfrac{2}{3} K_i c_i^3 \omega \qquad \text{(III.9)}$$

and

$$T_{2,a} = 4c_a^2 \omega(1 - \alpha^{-1}) + \tfrac{2}{3} K_a c_a^3 \alpha^{-3/4} \omega^{3/5} \qquad \text{(III.10)}$$

$$\ln c_i + 2c_i + T_{3,i} = \ln c_a + \sigma_a + 2c_a \rho_a + T_{3,a} \qquad \text{(III.11)}$$

with

$$T_{3,i} = c_i \omega(\pi + 3 + K_i c_i) \qquad \text{(III.12)}$$

and

$$T_{3,a} = 8c_a \omega(1 - \alpha^{-1}) + K_a c_a^2 \alpha^{-3/4} \omega^{3/5} \qquad \text{(III.13)}$$

We have written these expressions explicitly in order to show the relative effects of the virial coefficients. The perturbation functions T_i alter the original coexistence calculation: hence, we set $\alpha = \alpha_0 + \delta\alpha$, $c_a = c_{a,0} + \delta c_a$, $\rho_a(\alpha)$ $= \rho_a(\alpha_0) + \rho_a'(\alpha_0)\delta\alpha$, $\sigma'(\alpha) = \sigma'(\alpha_0) + \sigma''(\alpha_0)\delta\alpha$, where the δ-type terms are all assumed small. The zero-order terms $\rho'(\alpha_0) = -0.011\,996$, $\rho''(\alpha_0) = 0.000\,859\,58$ are calculated from eq II.26.

We now derive the first-order deviations from the original second virial approximation by simple elimination, keeping in mind that we set α, c_i, and c_a equal to their zero-order values in eq III.9–13

$$\delta c_i = -52\omega + 9.8\omega^{3/5}$$

$$\delta c_a = -123\omega + 33\omega^{3/5} \qquad \text{(III.14)}$$

$$\delta\alpha = -1590\omega + 660\omega^{3/5}$$

It is convenient to tabulate these results in their range of validity ($20 \lesssim \omega^{-1} \lesssim 50$). Since the $\delta\alpha$ values are quite large, the equations III.14 are only qualitative. Nonetheless, Table I shows that the effect of B_3 and end effects in B_2 in the concentration are never more than perturbative. The order parameter and density ratio are systematically shifted upward. These conclusions are in qualitative agreement with the fully numerical work of Straley.[19] The difference is due to Straley's possible neglect of end effects in B_2.

Table I
Change of the Composition and Parameter α at the Phase Transition Due to the Third Virial Coefficient as a Function of the Axial Ratio ω^{-1}

	ω^{-1}			
	20	30	40	50
δc_i	−1.0	−0.5	−0.2	−0.1
δc_a	−0.7	0.2	0.5	0.7
$\delta\alpha$	29	33	32	31

We conclude this section by stating that the Onsager theory based on the second virial approximation cannot always be quantitative in the practical range of ω values. However, the influence of the third virial coefficient is very much less than some would have us believe. End effects in B_2 must also be taken into account in any serious consideration of the effect of B_3. Evidently, more numerical work is needed.

IV. Bidisperse Rods

When the rodlike macromolecules are no longer monodisperse, the effect of polydispersity must be carefully analyzed. We first consider the relatively simple case of bidisperse rods: our solution contains N rods, of which N_1 have length L_1 and N_2 length L_2. (Index 1 will hereafter refer to the shorter rods, and index 2 to the longer ones.) All rods have the same diameter D. Again, c' is the total number density $N/V = (N_1 + N_2)/V$, and the mole fraction $x = N_2/N$ of longer rods is another convenient intensive variable. Provided the rods are long enough, half the random excluded volume b_{jk} between a pair of rods of types j and k is simply

$$b_{jk} = (\pi/4)L_j L_k D, \qquad j, k = 1, 2 \qquad \text{(IV.1)}$$

If the length ratio is defined as $q = L_2/L_1$ with $q \geq 1$, eq IV.1 is rewritten in terms of b

$$b_{11} = b$$

$$b_{12} = b_{21} = qb \qquad \text{(IV.2)}$$

$$b_{22} = q^2 b$$

Introducing the orientational distribution function $f_j(\Omega)$, we can now write the obvious generalization of eq II.2, II.3, II.11, and II.12

$$\int f_j(\Omega)\, d\Omega = 1 \qquad \text{(IV.3)}$$

$$\sigma_j = \int f_j(\Omega)\ln[4\pi f_j(\Omega)]\, d\Omega \qquad \text{(IV.4a)}$$
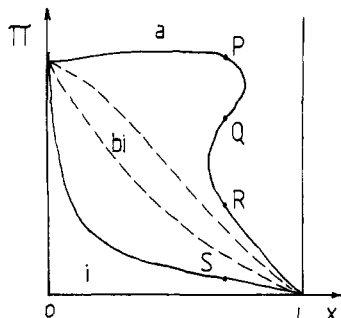
$$\rho_{jk} = \frac{4}{\pi}\int\int |\sin\gamma(\Omega,\Omega')| f_j(\Omega) f_k(\Omega')\, d\Omega\, d\Omega' \qquad \text{(IV.4b)}$$

$$\frac{\Delta F}{Nk_BT} = \frac{(1-x)\mu_1^\circ(T,\mu_0) + x\mu_2^\circ(T,\mu_0)}{k_BT} - 1 + \ln c' +$$
$$(1-x)\ln(1-x) + x\ln x + (1-x)\sigma_1 + x\sigma_2 + bc'\{(1-x)^2\rho_{11} + 2x(1-x)q\rho_{12} + x^2q^2\rho_{22}\} \qquad \text{(IV.5)}$$

The coupling term ρ_{12} causes deviations from the monodisperse case. If we minimize ΔF with respect to f_1 and f_2, we get

$$\ln[4\pi f_1(\Omega)] =$$
$$C_1 - \frac{8c}{\pi}\int |\sin\gamma(\Omega,\Omega')|[(1-x)f_1(\Omega') + xqf_2(\Omega')]\, d\Omega' \qquad \text{(IV.6a)}$$

$$\ln[4\pi f_2(\Omega)] =$$
$$C_2 - \frac{8qc}{\pi}\int |\sin\gamma(\Omega,\Omega')|[(1-x)f_1(\Omega') + xqf_2(\Omega')]\, d\Omega' \qquad \text{(IV.6b)}$$

Figure 1. Qualitative diagrams of the osmotic pressure Π vs. mole fraction x for mixtures of bidisperse rods: dashed lines, coexistence curves for length ratio q near unity; drawn lines, q much larger than unity. In the latter case reentrance can be seen in a sequence such as PQRS as the osmotic pressure decreases when the system is diluted.

where C_1 and C_2 are determined by eq IV.3 and $c = bc'$. We can easily eliminate f_2 from eq IV.6a,b

$$\ln\ (4\pi f_2) - C_2 = q[\ln\ (4\pi f_1) - C_1] \qquad \text{(IV.7)}$$

$$\ln\ [4\pi f_1(\Omega)] =$$

$$C_1 - \frac{8c}{\pi} \int \sin\ \gamma[(1 - x)f_1 + xq(4\pi)^{q-1}e^{C_2-qC_1}f_1{}^q] \quad \text{(IV.8)}$$

This highly nonlinear integral equation does not look all that pleasing. Nonetheless it is easy to establish that a stable anisotropic solution exists using the Kayser–Raveché recipe[17] outlined earlier. We simply write $4\pi f_1 = 1 + h$ and linearize eq IV.8 in h, and the resulting eigenvalue problem gives $h = P_2(\cos\ \theta)$ and $(1 - x + xq^2)c^* = 4$. We immediately see that a few longer rods can enhance stabilization of the nematic.

The coexistence equations (II.23) and (II.24) are also easily derived when the rods are bidisperse (index i = isotropic, index a = anisotropic)

$$c_i[1 + c_i(1 + (q - 1)x_i)^2] =$$
$$c_a[1 + c_a[(1 - x_a)^2\rho_{11} + 2x_a(1 - x_a)q\rho_{12} + x_a{}^2q^2\rho_{22}]]$$
$$\text{(IV.9)}$$

$$\ln\ c_i + \ln\ (1 - x_i) + 2c_i[1 + (q - 1)x_i] =$$
$$\ln\ c_a + \ln\ (1 - x_a) + \sigma_1 + 2c_a[(1 - x_a)\rho_{11} + x_aq\rho_{12}]$$
$$\text{(IV.10)}$$

$$\ln\ c_i + \ln\ x_i + 2c_iq[1 + (q - 1)x_i] =$$
$$\ln\ c_a + \ln\ x_a + \sigma_2 + 2c_aq[(1 - x_a)\rho_{12} + x_aq\rho_{22}] \quad \text{(IV.11)}$$

Several accurate numerical solutions of eq IV.6 and IV.9–11 have been given only recently. Because the hard-rod system is athermal there is one degree of freedom according to the Gibbs phase rule. Lekkerkerker et al.[20] solved the above equations for $q = 2$ and $q = 5$, choosing x_i as the independent variable, and we summarize their main results.[98]

1. $x_a > x_i$ (e.g., $x_i = 0.1$, $x_a = 0.741$ for $q = 5$). The longer rods are preferentially driven into the nematic phase. This preference increases with the length ratio.

2. The order parameter S_2 of the longer rods is almost always larger than the monodisperse one S_0.

3. S_1 of the shorter rods is larger than S_0 when x_a is small. For x_i and x_a both approaching unity, S_1 dips to a very low value (e.g., $S_1 = 0.192$ for $x_i = 0.9$ and $q = 5$).

4. Both S_1 and S_2 exhibit one maximum as a function of x_i.

5. The Π-x coexistence diagram changes its structure when we increase the length ratio q from 2 to 5 (see Figure 1). For $q = 5$ a reentrant phenomenon is predicted for a certain range of x_i. As we increase the total concentration we come across the following sequence of phases: iso-
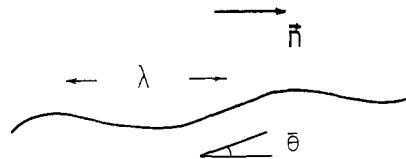
Figure 2. A wormlike chain under the influence of an average nematic field along **n**. The polymer is constrained within a typical angle $\bar{\theta} \simeq \alpha^{-1/2}$. The deflection length λ shows the scale on which the polymer is deflected from ideally wormlike paths in order to conform to this constraint.

tropic–biphasic–pure nematic–biphasic–pure nematic.

Bidispersity thus has a profound and rather unexpected effect on the isotropic–nematic phase transition. A semiquantitative analytical theory has been developed[21] that enables us to understand almost all of the above items found by numerical analysis. Here we highlight some of these calculations.

Since both S_1 and S_2 can apparently reach high values we simply use Gaussian trial functions with α_1 and α_2 for the respective species of rods (see eq II.14). In this approximation eq IV.12 is just the leading term derived in the appendix to ref 2.

$$\rho_{jk} = \frac{4(\alpha_1 + \alpha_2)^{1/2}}{(2\pi)^{1/2}\alpha_1{}^{1/2}\alpha_2{}^{1/2}} \qquad (\alpha_j, \alpha_k \gg 1; j, k = 1, 2)$$
$$\text{(IV.12)}$$

Minimization of eq IV.5 in the Gaussian approximation leads to an interesting set of coupled expressions[21]

$$\tfrac{1}{2}\pi^{1/2}c_a{}^{-1}\alpha_1{}^{1/2} = (1 - x_a) + 2^{1/2}x_aqh(Q) \quad \text{(IV.13)}$$

$$\tfrac{1}{2}\pi^{1/2}c_a{}^{-1}\alpha_2{}^{1/2} = 2^{1/2}(1 - x_a)qg(Q) + x_aq^2 \quad \text{(IV.14)}$$

with

$$Q \equiv \alpha_2/\alpha_1; \qquad g(z) \equiv (1 + z)^{-1/2};$$
$$h(z) \equiv \left(\frac{z}{z + 1}\right)^{1/2} \qquad \text{(IV.15)}$$

It can be seen at once that the terms h and g exert a remarkable influence on α_1 and α_2. Even though c_a can be eliminated, Q cannot be obtained explicitly. However, it can be shown that Q is a bounded and monotonically increasing function of x_a.[21]

$$\tfrac{1}{2}(8q^2 + 1)^{1/2} - \tfrac{1}{2} \leqslant Q \leqslant \tfrac{1}{4}q^2[1 + (1 + 8q^{-2})^{1/2}] \quad \text{(IV.16)}$$

The the longer rods are always more highly ordered than the shorter ones.

Solving eq IV.9–15 analytically looks like a hopeless task. Nevertheless, there are two major simplifications: (a) from a physical point of view an interesting region is $x_iq \ll 1$; (b) the nematic excluded volume term η in eq IV.9 simplifies to a pure number after repeated rearrangements using eq IV.12–16.[21]

$$\eta = c_a[(1 - x_a)^2\rho_{11} + 2x_a(1 - x_a)q\rho_{12} + x_a{}^2q^2\rho_{22}] = 2$$
$$\text{(IV.17)}$$

Accordingly, c_a is completely slaved to c_i via the osmotic pressure eq IV.9

$$c_i + c_i{}^2 = 3c_a \qquad (x_iq \ll 1) \qquad \text{(IV.18)}$$

This expression is surely unexpected. Provided $x_iq \ll 1$, we can state that whatever the values of q and x_a, the concentrations are connected by a form completely identical with that valid for the monodisperse case (denoted by index zero; see eq II.17, II.20, and II.23)

$$c_{i,0} + c_{i,0}{}^2 = 3c_{a,0} \qquad \text{(IV.19)}$$

Table II
Values of the Quantity p Described in the Text[a] As
Calculated from Tables II and III of Ref 20

x_i	$q = 2$	$q = 5$
0	1.123	1.123
0.1	1.047	1.072
0.2	1.056	1.027
0.3	1.067	0.997
0.4	1.076	1.000
0.5	1.086	1.011
0.6	1.093	1.029
0.7	1.102	1.058
0.8	1.109	1.074
0.9	1.116	1.092

[a] In the Gaussian approximation p is equal to unity.

We can gauge the accuracy of $\eta = 2$ by considering numerical values of the variable $p \equiv [c_i + c_i^2(1 + (q - 1)x_i)^2](3c_a)^{-1}$, which should be equal to unity by eq IV.9 and eq IV.17.[24] The quantity p is shown in Table II as a function of x_i and q, the numerical c_i and c_a values being taken from Tables II and III of ref 20. The Gaussian approximation evidently works rather well.

The independent variable is now conveniently chosen to be x_a. Equation IV.10 can then be rearranged as follows if we taken account of eq II.18, IV.12, IV.13, and IV.19.

$$j(c_i) = \varphi(x_a, q, Q(x_a, q)) \tag{IV.20}$$

The properties of j and φ turn out to be as follows.[21] The function j has only one minimum (=−0.628 for $c_{i,m} = 2$) and goes to infinity as $c_i \to 0$ or $c_i \to \infty$. If $x_a = 0$, then $\varphi = 0$ and $j = 0$ so that $c_i = c_{i,0}$ or $c_i = c^*_{i,0}$ (the concentrations in the Gaussian approximation given in section II). Although very complicated the function φ is usually bounded in the range of interesting q and x_a values. We have the following scheme:

(a) $\varphi < j(c_{i,m})$: no solution. This happens for x_a approaching unity.

(b) $\varphi = j(c_{i,m})$: one solution; x_a and q relatively large.

(c) $\varphi > j(c_{i,m})$: two solutions; both are stable when x_a is near unity and q is large. Equation II.27 is now $1 + \ln \alpha_1 + x_a \ln Q < c_a(1 - x_a + x_a q)^2$. Hence the c^*-type solution is sometimes admissible. The possibility of two solutions (or more if $x_i \to 1$) shows that reentrance must occur.

Purely for numerical reasons φ is often positive for quite large x_a.[21] Equation IV.20 then implies that $c_i > c_{i,0} = 3.45$ or $c_a > c_{a,0} = 5.1$. Hence from eq IV.13 and IV.14

$$\alpha_1 = \mathcal{O}(x_a^2 q^2 c_a^2)$$

$$\alpha_2 = \mathcal{O}(x_a^2 q^4 c_a^2)$$

For instance, if $x_a = 0.7$ and $q = 5$, the α parameters are exceedingly high; viz., $\alpha_1 = \mathcal{O}(10^3)$, $\alpha_2 = \mathcal{O}(10^4)$.

Odijk and Lekkerkerker[21] also treated other facets of the influence of bidispersity, e.g. the case of $(q - 1) \ll 1$ but we refer the reader to their paper.

We end this section with three remarks. First, bidispersity can greatly enhance the stability of the first-order transition. From eq IV.5, IV.13, and IV.17 we can see that the stabilization per rod is given by the following lower bound:

$$\frac{\Delta F_i(c_a, x_a) - \Delta F_a(c_a, x_a)}{Nk_BT} \geq c_a(1 - x_a + x_a q)^2 -$$

$$\ln\left(\frac{4eq^2 c_a}{\pi}\right) c_a(1 - x_a + x_a q)^2$$

The right-hand side can easily be of the order of 10. By contrast, for monodisperse rods the stabilization energy

per rod is only $0.222\ k_BT$ and so the isotropic–nematic transition is weakly first order.[94] It has been conjectured[23] that the weakness of the transition is connected with the small parameter $\omega = D/L$. However, in the Onsager approach the stabilization is independent of ω if it is small enough. Because the rods can be throught of as enclosed within cylinders of length L and diameter $L\langle\theta^2\rangle^{1/2}$, a better parameter characterizing the transition is probably $\alpha^{-1/2}$. This quantity could easily decrease by a factor of 20 because of bidispersity, thus increasing stabilization.

Next, we note that eq IV.9 and IV.17 show that there is one and only one value of c_a compatible with a given set (c_i, x_i). This implies that only one anisotropic phase is possible. Even though the Gaussian approximation is the premise of this conclusion, it cannot be dismissed too lightly as Table II shows.

Finally we comment on the validity of using only the $\omega_j \to 0$ asymptotic limit. Equations III.2–5 show that we require

$$\omega_1 \ll \alpha_1^{-1/2}$$

$$\omega_2 \ll \alpha_2^{-1/2}$$

if we do not want to take along B_3 and particularly end effects in B_2, in a first approximation.

V. Polydisperse Rods

We are not aware of any work within the Onsager approach that systematically solves the coexistence equations while taking account of polydispersity (although some qualitative work by McMullen et al. has appeared recently[97]). To see what kind of problems we are up against let us very briefly review the equations that need a solution.

Equation IV.5 is immediately generalized to

$$\frac{\Delta F}{Nk_BT} = \sum_j (x_j \mu_j^\circ / k_BT) - 1 + \ln c' + \sum_j x_j \ln x_j + \sum_j \sigma_j x_j + bc' \sum_j \sum_k x_j x_k q_j q_k \rho_{jk} \tag{V.1}$$

Here the indices j and k refer to any two of the M different species of rods, μ_j° is the standard chemical potential of rod j, x_j is the mole fraction of rods of type j, the length ratio $q_j = L_j/L_1$ is taken with respect to the length L_1 of the shortest rods, and b is as defined before. In section IV we argued that the Gaussian approximation works rather well for bidisperse and by implication polydisperse rodlike macromolecules. Thus we use it also in this section: we have $\sigma_j(\alpha_j) \sim \ln \alpha_j - 1$ from eq II.18 and ρ_{jk} given by eq IV.12.

For the nematic phase the extremalization of ΔF with respect to α_k gives an equation analogous to eq IV.13 and IV.14[24]

$$\tfrac{1}{2}\pi^{1/2}c_a^{-1}\alpha_k^{1/2} = 2^{1/2}\sum_j x_{a,j} q_j q_k g(Q_{kj}), \qquad k, j = 1...M \tag{V.2}$$

where $Q_{kj} = \alpha_k/\alpha_j$. Note that the ordering of the indices of the quantity Q_{kj} is essential. Furthermore, these M equations are coupled to each other. The scaled concentration can be eliminated

$$Q_{kj}^{1/2} = \frac{\sum_n x_{a,n} q_n q_k g(Q_{kn})}{\sum_m x_{a,m} q_m q_j g(Q_{jm})} \tag{V.3}$$

One can prove that the analogue of eq IV.17 is again equal to 2.[24]

$$\eta = c_a \sum_j \sum_k x_{a,j} x_{a,k} q_j q_k \rho_{jk} = 2 \tag{V.4}$$

Hence the scaled osmotic pressure is given by

$$\Pi_a = 3c_a \qquad (V.5)$$

and the osmotic pressure coexistence equation is

$$c_i\left(1 + c_i\sum_j\sum_k x_{i,j}x_{i,k}q_jq_k\right) = 3c_a \qquad (V.6)$$

Differentiation of eq V.1 with respect to N_i yields M coexistence equations associated with the chemical potentials of each of the species

$$\ln c_i + \ln x_{i,k} + 2c_i\sum_l x_{i,l}q_kq_l =$$
$$\ln c_a + \ln x_{a,k} + \sigma_{a,k} + 2c_a\sum_l x_{a,l}q_kq_l\rho_{kl}, \qquad k = 1...M$$
$$(V.7)$$

Equations IV.12, V.2, V.6, and V.7 are a formidable set of coupled algebraic equations although the example of eq V.4 shows that simplification could be possible. For now we just prove that in the nematic phase longer rods are always more highly ordered than shorter ones. We rewrite eq V.3

$$Q_{kj}^{1/2} = \frac{q_k g(Q_{kj})}{q_j}\left[\frac{1 + \sum_{n\neq j}\left(\frac{x_nq_n}{x_jq_j}\right)\left(\frac{g(Q_{kn})}{g(Q_{kj})}\right)}{1 + \sum_{m\neq j}\left(\frac{x_mq_m}{x_jq_j}\right)(g(Q_{jm}))}\right] =$$

$$\frac{q_k g(Q_{kj})}{q_j}\left[1 + \frac{\sum_{n\neq j}\left(\frac{x_nq_n}{x_jq_j}\right)\left(\frac{g(Q_{kn})}{g(Q_{kj})} - g(Q_{jn})\right)}{1 + \sum_{m\neq j}\left(\frac{x_mq_m}{x_jq_j}\right)g(Q_{jm})}\right]$$

It is easy to show that $g(Q_{kn})g^{-1}(Q_{kj}) - g(Q_{jn}) > 0$. Hence we have

$$Q_{kj} > \frac{1}{2}\left(\frac{4q_k^2}{q_j^2} + 1\right)^{1/2} - 1$$

When $q_k \gg q_j$, we have concomitantly $\alpha_k \gg \alpha_j$.

VI. Rodlike Polyelectrolytes

The influence of charge on the isotropic–nematic transition is twofold: (1) the effective diameter increases by an amount approximately proportional to the double-layer thickness, an effect that is incidentally not exactly the same in the two phases; (2) two test rods exert a twisting force on each other. A detailed numerical and analytical theory has only recently been proposed.[22,96] It is summarized below.

In the evaluation of cluster expansions we only need to a first approximation the potential w_0 between the outer double layers of two rodlike polyelectrolytes. This has the general form[22,25-27,95]

$$\frac{w}{k_BT} = \frac{Ae^{-\kappa x}}{\sin\gamma} \qquad (VI.1)$$

Here, x is the shortest distance between the center lines of the rods, κ^{-1} is the Debye–Hückel screening radius, and A is a parameter that depends on the polyion properties and is discussed at length in ref 22. The angle-dependent electrostatic second virial coefficient is given by [2,22]

$$B_{2,el}(\gamma) = 2L^2\sin\gamma\int_D^\infty(1 - e^{-w/k_BT})\,dx \simeq$$
$$\frac{2L^2\sin\gamma}{\kappa}[\ln A' + C_E - \ln|\sin\gamma|] \quad (VI.2)$$

where C_E is Euler's constant and $A' = Ae^{-\kappa D}$ must be larger than 2. Equation VI.2 illustrates the increase in diameter of order κ^{-1} and the effect of twist $(-\ln|\sin\gamma|)$. The latter term forces us to revise the theory of section II. In this case it is particularly convenient to rescale the variables in such a way that the free energy is written in the usual form (using eq II.1, II.2, II.8–12, and VI.2)[22]

$$\frac{\Delta F}{Nk_BT} = \frac{\mu^\circ}{k_BT} - 1 + \ln c' + \sigma(f) + \tilde{b}c'(\rho(f) + h\eta(f)) \qquad (VI.3)$$

with

$$\tilde{b} = (\pi/4)L^2\tilde{D} \qquad (VI.4)$$

$$\tilde{D} = D(1 + \delta) \qquad (VI.5)$$

$$\delta = (\kappa D)^{-1}(\ln A' + C_E + \ln 2 - \tfrac{1}{2}) \qquad (VI.6)$$

$$h = (\kappa\tilde{D})^{-1} \qquad (VI.7)$$

$$\eta(f) = (4/\pi)\langle-|\sin\gamma|\ln|\sin\gamma|\rangle - (\ln 2 - \tfrac{1}{2})\rho \qquad (VI.8)$$

In the isotropic solution $\eta_i = 0$ because $\langle-|\sin\gamma|\ln|\sin\gamma|\rangle_i = (\pi/4)(\ln 2 - \tfrac{1}{2})$. Since all equations will be written in terms of the scaled concentrations $c = \tilde{b}c'$, the twisting effect depends on the parameter h and on this combination of A, κ, and D only. The dependence of δ on κ is such that h is at most about 0.5. Conceivably a perturbation calculation should work and it is in fact very similar to that outlined in section III. Using eq VI.8 and trial function eq II.13 one can derive $\eta(\alpha)$ after a tedious asymptotic expansion.[22] Minimizing eq VI.3 yields an expression relating the twisting force to the usual confinement and excluded volume effect.[22]

$$\sigma'(\alpha) + c_a(\rho'(\alpha) + h\eta'(\alpha)) = 0 \qquad (VI.9)$$

The extension of the coexistence eq II.23 and II.24 is written down at once

$$c_i(1 + c_i) = c_a[1 + c_a(\rho_a + h\eta_a)] \qquad (VI.10)$$

$$\ln c_i + 2c_i = \ln c_a + \sigma_a + 2c_a(\rho_a + h\eta_a) \quad (VI.11)$$

A perturbation scheme around the zero-order hard-rod fluid is straightforward. As in section III one introduces $c_i = c_{i,0} + \delta c_i$, $\rho'(\alpha) = \rho'(\alpha_0) + \rho''(\alpha_0)\delta\alpha$, and so forth. The result is

$$\delta c_i = 2.37h$$
$$\eta c_a = 3.01h \qquad (VI.12)$$
$$\delta\alpha = 21.3h$$

Detailed numerical calculations show that eq VI.12 work rather well for $h \lesssim 0.15$. Higher values demand computer calculations.[22] The numerical work is similar to that described in section II. (But see also ref 96.) Equation VI.8 can be expanded in Legendre polynomials. Convergence is somewhat more difficult to obtain than for the case of purely hard rods. This is not surprising in view of the fact that the Legendre expansion of the twisting term yields a slowly varying series. When $h \gtrsim 0.15$ eq VI.12 underestimates the computer solution, the margin becoming marked when $h = 0.4$ (the numerical values are then $\delta c_i = 1.492$, $\delta c_a = 2.491$, $\delta\sigma = 1.351$, and $\delta S = 0.146$).

The dimensionless variable h has in general a very complicated dependence on ionic strength and polyion parameters.[22] In practice, values of h higher than about 0.5 do not occur—this is for weakly charged polyelectrolytes (say a charge density of about 1 electron charge/2 nm viewed along the axis). The scaled concentrations can be about 50% higher than those calculated assuming an effective hard-rod model. For highly charged polyelec-

trolytes typical values of h are about 0.15, implying a small but significant twisting effect as can be seen from eq VI.12. Why the effect of twist is larger for weakly charged polymers can be understood from eq VI.2: the twisting effect remains constant when we decrease the polyion charge density whereas the effective diameter decreases via A'.

Lastly, the expression for the bifurcation density calculated in the same way as previously is rather interesting

$$c^*(1 - \tfrac{3}{4}h) = 4 \qquad (VI.13)$$

If h were to reach $^4/_3$, the twisting effect would effectively destabilize the nematic phase. Within the restrictions of the calculation of ref 22 it does not seem possible to ever attain this value. It would nevertheless be interesting to see whether charge destabilization might occur under different circumstances (e.g., for relatively short polyions). Equation VI.13 also alludes to a semiempirical way of expressing the numerical results of Stroobants et al.[22]

$$c_a = 4.191(1 - 0.730h)^{-1}$$

$$c_i = 3.290(1 - 0.675h)^{-1} \qquad (VI.14)$$

These formulas describe the values of Table III in ref 22 quite closely. For small h we essentially regain eq VI.12.

VII. Bidisperse Rodlike Polyelectrolytes

Here we briefly investigate the coupling of bidispersity and the twisting effect. Equations IV.5 and VI.3 can be generalized to the case of bidisperse charged rods

$$\frac{\Delta F}{Nk_B T} = \frac{(1 - x)\mu_1°(T,\mu_0) + x\mu_2°(T,\mu_0)}{k_B T} - 1 + \ln c' +$$
$$(1 - x)\ln(1 - x) + x \ln x + (1 - x)\sigma_1 + x\sigma_2 + bc'\{(1 - x)^2\xi_{11} + 2x(1 - x)q\xi_{12} + x^2 q^2 \xi_{22}\} \quad (VII.1)$$

with

$$\xi_{kl} = \rho_{kl}(f) + h\eta_{kl}(f) \qquad (VII.2)$$

The twisting term η_{kl} is given in the Gaussian approximation by

$$\eta(\alpha_k, \alpha_l) = \frac{2}{\pi^{1/2}}\left(\frac{\alpha_k + \alpha_l}{2\alpha_k \alpha_l}\right)^{1/2}\left[\ln\left(\frac{2\alpha_k \alpha_l}{\alpha_k + \alpha_l}\right) - 2\ln 2 - 1 + C_E\right] \quad (k, l = 1, 2; \alpha_k, \alpha_l \gg 1) \quad (VII.3)$$

This is obtained by asymptotically expanding an integral of the type

$$\langle -\sin\gamma \ln(\sin\gamma)\rangle_a = \tfrac{1}{2}(\sinh\alpha_1 \sinh\alpha_2)^{-1} \times$$
$$\int_{\gamma=0}^{\pi}\cosh[\alpha_1^2 + \alpha_2^2 + 2\alpha_1\alpha_2 \cos\gamma]^{1/2} d(-\sin\gamma \ln(\sin\gamma))$$

When $\alpha_k = \alpha_l$, eq VII.3 reduces to the leading term of the expansion for monodisperse polyelectrolytes.[22] Minimization of eq VII.1 gives

$$\tfrac{1}{2}\pi^{1/2}c_a^{-1/2}\alpha_1^{1/2} = (1 - x)(1 + \tfrac{1}{2}hY) +$$
$$2^{1/2}xqg(Q^{-1})\left[1 + \tfrac{1}{2}h\left(Y + \ln\left(\frac{2Q}{1 + Q}\right)\right)\right] \quad (VII.4)$$

$$\tfrac{1}{2}\pi^{1/2}c_a^{-1}\alpha_2^{1/2} = 2^{1/2}(1 - x)qg(Q)\left[1 + \tfrac{1}{2}h\left(Y + \ln\left(\frac{2Q}{1 + Q}\right)\right)\right] + xq^2[1 + \tfrac{1}{2}h(Y + \ln Q)] \quad (VII.5)$$

with $Y \equiv \ln \alpha_1 - 2\ln 2 - 3 + C_E$. We have seen that the twisting parameter h can be about 0.5 and bidispersity may

lead to enhanced ordering with $\alpha_1 = \mathcal{O}(10^3)$. Accordingly, charge and bidispersity together could give rise to qualitatively different behavior from that due to only one of the effects. The presence of logarithmic terms makes the problem rather delicate so that numerical work on this problem is called for.

VIII. Semiflexible Polymers

Till now we have been focusing attention on modifications and extensions of the excluded-volume effect in eq II.1. However, when the rods are no longer completely rigid the calculation of $\sigma(f)$ is far from trivial and becomes the main problem. A convenient treatment of $\sigma(f)$ was first given by Khokhlov and Semenov.[28,29] It is the author's impression that this theory is not well understood so the semiflexibility effect is documented thoroughly here by appealing to several theoretical viewpoints. This also enables us to reach a consensus on the physics of confined chains and surfaces.

(a) **Scaling Theory.** We consider a solution of volume V containing N long wormlike cylinders of contour length L, persistence length P, and diameter D ($L \gg P \gg D$). The concentration $c' = N/V$ is so high that the excluded-volume effect causes nematic ordering along the director $\mathbf{n}$. We disregard end effects for the moment; it is thus possible to assign the same orientational distribution function $f(\theta)$ to every unit tangent vector $\mathbf{u}(s)$ along some test curve ($0 \leq s \leq L$; θ is the angle between $\mathbf{n}$ and $\mathbf{u}(s)$). Let us assume f is again of the Gaussian type (see eq II.14)—we are assuming only leading-order behavior. For convenience we write again

$$\langle\theta^2\rangle = 2\alpha^{-1} \qquad (\alpha \gg 1) \qquad (VIII.1)$$

This can be viewed as a restriction imposing a certain degree of orientational order on the wormlike polymer.

We now follow the arguments of a recent scaling theory.[30] If the test chain were unconfined, we would have the usual expression for the orientational correlation function[31,32]

$$\langle\mathbf{u}(s)\cdot\mathbf{u}(t)\rangle = \langle\cos\theta(t - s)\rangle = \exp(-|t - s|/P) \quad (VIII.2)$$

When the angle $\theta(t - s)$ between the unit vectors $\mathbf{u}(s)$ and $\mathbf{u}(t)$ is small we have

$$\langle\theta^2(t - s)\rangle \simeq \frac{|t - s|}{P} \qquad (|t - s| \lesssim \tfrac{1}{3}P) \quad (VIII.3)$$

If $\mathbf{u}(s)$ is in the direction of $\mathbf{n}$, eq VIII.3 will hold until the restraint eq VIII.1 starts coming into play, i.e. when $\langle\theta^2(t - s)\rangle \simeq \langle\theta^2\rangle$. This fixes a length scale called the deflection length[30,33]

$$\lambda \equiv P/\alpha \qquad (VIII.4)$$

Hence, if $|t - s| \lesssim \lambda$ the fluctuations are governed more or less by the statistics of an unconfined chain, in other words, elastic bending energy vs. thermal energy. Whenever $|t - s| \gg \lambda$, eq VIII.2 and VIII.3 break down completely because then a nematic correlation persists embodied in eq VIII.1. The nematic field deflects the chain so that angular deviations from $\mathbf{n}$ remain within a cone of angle approximately equal to $\alpha^{-1/2}$ (see Figure 2). For long chains the persistence length is no longer of importance. In fact we can state that the confinement free energy or σ of a test chain is a function of L, λ, and possibly α. The free energy must be extensive or proportional to the contour length L so that

$$\sigma = (L/\lambda)g(\alpha) \qquad (VIII.5)$$

The worm can be viewed as a sequence of L/λ links each of length λ, the factor $g(\alpha)$ specifying the negative con-

finement entropy of every link. If we simply disregard all fluctuations except those of about a wavelength λ, g is just the negative orientational entropy of a rod (eq II.18)

$$g \simeq \ln \alpha \qquad \text{(VIII.6)}$$

However, the scaling approach does not give us a complete picture of the fluctuations. In fact, logarithmic terms are always hard to deduce by scaling arguments. In the following section we prove

$$g = \text{constant} \qquad \text{(VIII.7)}$$

Equations VIII.4, VIII,5, and VIII.7 yield

$$\sigma = (L/P)\alpha \qquad \text{(VIII.8)}$$

This rather surprising proportionality to α should be contrasted with another expression thought[9] to describe confined stiff chains well

$$\sigma_{\mathrm{I}} = (L/P) \ln \alpha \quad \text{(incorrect)}$$

$$\sigma_{\mathrm{I}} \ll \sigma \qquad (\alpha \gg 1) \qquad \text{(VIII.9)}$$

To arrive at eq VIII.9 one arbitrarily assumes that a nematic wormlike polymer can be viewed as a sequence of L/P rigid links of length P. By contrast, the actual typical angle between the tangential end vectors of a persistence length section is about 1.2 radians, an angle considerably larger than that of eq VIII.1. Hypothetically straightening out sections of about a persistence length before calculating the orientational free energy will just not do.

(b) Fluctuation Theory. Helfrich[34-36] has devised methods to calculate the so-called undulation force between two or more membranes in close proximity. The thermal fluctuations of each membrane surface are restricted when two such surfaces approach, which leads to an increasing confinement free energy, and hence an undulation force. Clearly a connection between this problem and the one discussed above exists. Using scaling agreements the author calculated the free energy of a wormlike chain enclosed within a tube[33] and this is, apart from a spurious logarithmic factor, equivalent to an expression recently derived by Helfrich and Harbich.[36] Here we simply apply the Helfrich line of reasoning to nematically confined wormlike polymers.

We shall include only small orientational fluctuations away from the director oriented along the z axis in our Cartesian coordinate system. This is valid in the nematic state in view of eq VIII.1, but for the unconfined chain we introduce some error when calculating the free energy. Nevertheless, this error is at most of order $(L/P)k_\mathrm{B}T$ because we neglect long-wavelength fluctuations with $|s - t| \gtrsim {}^1\!/_3 P$. This is smaller than the terms we retain. Accordingly, we write[31,32]

$$\Delta F_\mathrm{b} = \frac{1}{2} Pk_\mathrm{B}T \int_0^L ds \left[\left(\frac{d\theta_x}{ds} \right)^2 + \left(\frac{d\theta_y}{ds} \right)^2 \right] \qquad \text{(VIII.10)}$$

for the bending (free) energy of a configuration described by $u_x \simeq \theta_x$, $u_y \simeq \theta_y$, $u_z \simeq 1$ in our coordinate system ($\mathbf{u}(s)$ and $\theta(s)$ were described in section VIII.a). As is often done in the theory of fluctuations[31] we introduce a Fourier expansion

$$\theta_j = \sum_q \theta_{j,q} e^{iqs}, \qquad j = x, y \qquad \text{(VIII.11)}$$

so that eq VIII.10 yields for the configurational average of the bending energy of the qth mode

$$\langle \Delta F_{\mathrm{b},q} \rangle = {}^1\!/_2 Pk_\mathrm{B}TL\langle |\theta_q|^2 \rangle q^2 \qquad \text{(VIII.12)}$$

with

$$\langle |\theta_q|^2 \rangle = \langle |\theta_{x,q}|^2 \rangle + \langle |\theta_{y,q}|^2 \rangle$$

By the equipartition theorem $\langle \Delta F_{\mathrm{b},q} \rangle$ must equal $k_\mathrm{B}T$ for two degrees of freedom, so that the unconfined fluctuations are given by

$$\langle |\theta_q|^2 \rangle_{\text{free}} = 2(PLq^2)^{-1} \qquad \text{(VIII.13)}$$

We estimate the effect of nematic confinement by using an elegant device due to Helfrich.[34] One can argue that a force constant should be inversely proportional to the square of the angular deviations. Moreover, a restriction like (VIII.1) acts equally on the macromolecular fluctuations of every wavelength, its action being accounted for by the as yet unknown constant τ in the following balance of forces:

$$\langle |\theta_q|^2 \rangle^{-1}{}_{\text{nem}} = \langle |\theta_q|^2 \rangle^{-1}{}_{\text{free}} + \tau = {}^1\!/_2 PLq^2 + \tau \qquad \text{(VIII.14)}$$

Thus we can derive the average fluctuations by summing over all modes in a continuum approximation

$$\langle \theta^2 \rangle_{\text{nem}} = \sum_q \langle |\theta_q|^2 \rangle_{\text{nem}} = \left(\frac{L}{2\pi} \right) \int_{-\infty}^{\infty} dq \, ({}^1\!/_2 PLq^2 + \tau)^{-1} = \left(\frac{L}{2P\tau} \right)^{1/2} \qquad \text{(VIII.15)}$$

This must be equivalent to eq VIII.1; hence we have

$$\tau = \alpha^2 L/8P \qquad \text{(VIII.16)}$$

The confinement free energy is calculated with the help of a plausible expression for the free energy of two modes[34]

$$\langle \Delta F_q \rangle = k_\mathrm{B}T \ln \frac{\langle |\theta_q|^2 \rangle_{\text{free}}}{\langle |\theta_q|^2 \rangle_{\text{nem}}} \qquad \text{(VIII.17)}$$

Equations VIII.13, VIII.14, VIII.16, and VIII.17 give

$$\sigma = \langle \Delta F \rangle / k_\mathrm{B}T = \left(\frac{L}{2\pi} \right) \int_{-\infty}^{\infty} dq \, \ln \left(1 + \frac{\alpha^2}{4P^2q^2} \right) = \frac{\alpha L}{4P} = \frac{L}{4\lambda} \qquad \text{(VIII.18)}$$

The logarithm disappears on integrating by parts. Apparently there are enough fluctuations of wavelength longer than λ to cause its disappearance. The complete restriction to modes with $q \simeq \lambda^{-1}$ would give eq VIII.6 but this is out of the question.

(c) Analogy with Quantum Harmonic Oscillator. Let us simulate the effect of confinement by putting the test wormlike polymer in an external potential U_{ex}. The total free energy of a chain in a certain configuration ($\theta_x(s)$, $\theta_y(s)$, $0 \leqslant s \leqslant L$) is given by

$$\Delta F/k_\mathrm{B}T = U_{\text{ex}}/k_\mathrm{B}T + \Delta F_\mathrm{b}/k_\mathrm{B}T = \frac{\Gamma}{2P} \int_0^L (\theta_x{}^2 + \theta_y{}^2) \, ds + \frac{1}{2} P \int_0^L \left[\left(\frac{d\theta_x}{ds} \right)^2 + \left(\frac{d\theta_y}{dx} \right)^2 \right] ds \qquad \text{(VIII.19)}$$

where Γ is a dimensionless parameter that is to be determined. Using the vector notation $\theta = (\theta_x, \theta_y)$, we can write the partition function $Z(\theta_1, \theta_2, L)$ with the chain ends fixed as a functional integral over all configurations (assuming the bending fluctuations are small)

$$Z(\theta_1, \theta_2, L) = \int_{\theta(0)=\theta_1}^{\theta(L)=\theta_2} \mathcal{D}[\theta(s)] \exp\left(-\frac{1}{2}P \int_0^L \theta'^2 \, ds - \frac{1}{2}\Gamma P^{-1} \int_0^L \theta^2 \, ds \right) \qquad \text{(VIII.20)}$$

This is formally analogous to the density matrix of a

two-dimensional quantum harmonic oscillator[37] with the equivalence $m/\hbar \triangleq P$, $m\omega^2\hbar^{-1} \triangleq \Gamma P^{-1}$, $\hbar(k_BT)^{-1} \triangleq L$, $\mathbf{r}_i = (x_i,y_i) \triangleq \theta_i$, and $t \triangleq s$, with m the mass, ω the circular frequency, t time, and $\mathbf{r}$ the coordinates of the oscillator.

Using this analogy, we can deduce a faster version of the fluctuation theory. The Fourier expansion (eq VIII.11) and the equipartition theorem give

$$\langle |\theta_q|^2 \rangle = 2(PLq^2 + \Gamma LP^{-1})^{-1} \qquad \text{(VIII.21)}$$

On the one hand, we now have

$$\left\langle \int_0^L \theta^2 \, ds \right\rangle = L\sum_q \langle |\theta_q|^2 \rangle = L\Gamma^{-1/2} \qquad \text{(VIII.22)}$$

On the other, from eq VIII.1,

$$\left\langle \int_0^L \theta^2 \, ds \right\rangle = \int_0^L \langle \theta^2 \rangle \, ds = 2L\alpha^{-1} \qquad \text{(VIII.23)}$$

which implies

$$\Gamma = \tfrac{1}{4}\alpha^2 \qquad \text{(VIII.24)}$$

For the harmonic oscillator we know $\langle$kinetic energy$\rangle$ = $\langle$potential energy$\rangle$: accordingly, we get an expression identical with eq VIII.18 since by analogy $\langle \Delta F_b \rangle = \langle U_{ex} \rangle$

$$\sigma = \mathcal{F}/k_BT - \langle U_{ex}/k_BT \rangle = \tfrac{1}{2}\langle \Delta F/k_BT \rangle = \frac{\alpha L}{4P} = \frac{L}{4\lambda} \qquad \text{(VIII.25)}$$

Note that in this case the total free energy $\mathcal{F}$ is essentially equivalent to $\langle \Delta F \rangle$.[92]

A roundabout but nevertheless instructive route from eq VIII.20 to eq VIII.25 is to use the exact solution[37] to eq VIII.20

$$Z(\theta_1,\theta_2,L) = \left(\Gamma^{1/2}(2\pi)^{-1} \sinh^{-1}\left(\frac{L\Gamma^{1/2}}{P} \right) \right) \times$$
$$\exp\left\{ \left(-\frac{\Gamma^{1/2}}{2\sinh\left(\dfrac{L\Gamma^{1/2}}{P}\right)} \right) \left[(\theta_1^2 + \theta_2^2) \cosh\left(\frac{L\Gamma^{1/2}}{P} \right) - 2\theta_1 \cdot \theta_2 \right] \right\} \qquad \text{(VIII.26)}$$

For $L\Gamma^{1/2}P^{-1} \gg 1$ (i.e., $L \gg \lambda$) the partition function reduces to

$$Z(\theta_1,\theta_2,L) \sim \Gamma^{1/2}\pi^{-1} \exp\left[-\frac{L\Gamma^{1/2}}{P} - \frac{1}{2}\Gamma^{1/2}(\theta_1^2 + \theta_2^2) \right] \qquad \text{(VIII.27)}$$

The distribution of the angle θ for all points of the chain except those very close to the ends is simply

$$f(\theta) = \frac{\displaystyle\int d\theta_1 \int d\theta_2 \int_0^L dl \, Z(\theta_1,\theta,l)Z(\theta,\theta_2,L-l)}{L\displaystyle\int d\theta_1 \int d\theta_2 Z(\theta_1,\theta_2,L)} = \left(\frac{\Gamma}{\pi^2} \right)^{1/2} \exp(-\Gamma^{1/2}\theta^2) \qquad \text{(VIII.28)}$$

whence

$$\langle \theta^2 \rangle = \Gamma^{-1/2} \qquad \text{(VIII.29)}$$

so that we come back to eq VIII.24 again. Equation VIII.29 gives us $\langle U_{ex} \rangle = (L\alpha/(4P))k_BT$ and eq VIII.27 the total free energy $\mathcal{F}$

$$\mathcal{F}/k_BT = -\ln Z_{tot} = -\ln \int \int d\theta_1 \, d\theta_2 \, Z(\theta_1,\theta_2) = L\Gamma^{1/2}/P = L\alpha/(2P) \qquad \text{(VIII.30)}$$

Hence, we regain eq VIII.25

$$\sigma = \mathcal{F}/k_BT - \langle U_{ex}/k_BT \rangle = \alpha L/(4P) = L/(4\lambda) \qquad \text{(VIII.31)}$$

Note that one must be careful to exclude the external potential from the confinement free energy, which is associated only with the bending energy.

(d) Khokhlov–Semenov Theory. The wormlike chain is the continuous version of the freely rotating chain consisting of M_l links of length a with bond angle θ_f between adjacent links in such a way that[32]

$$\lim_{\substack{M \to \infty \\ a \to 0}} M_l a = L \qquad \text{(VIII.32)}$$

$$\lim_{\substack{a \to 0 \\ \theta_f \to \pi}} \left(\frac{a}{1 + \cos\theta_f} \right) = \lim \left(\frac{2a}{(\pi - \theta_f)^2} \right) = P \qquad \text{(VIII.33)}$$

The freely rotating polymer is put into an external field $U_{ex}(\mathbf{u})$ which would be exerted per unit length on some small rod oriented at angle $\mathbf{u}$ (note that U_{ex} of section VIII.c pertained to the whole polymer). Its links are denoted by the unit vector $\mathbf{u}_j$ ($j = 1, ..., M_l$). If θ_f is close to π the partition function $Z(\mathbf{u}_1,\mathbf{u}_{j+1})$ can be given in terms of a Taylor expansion

$$Z(\mathbf{u}_1,\mathbf{u}_{j+1}) = Z(\mathbf{u}_1,\mathbf{u}_j) + \tfrac{1}{4}(\mathbf{u}_{j+1} - \mathbf{u}_j)^2 \Delta_{\mathbf{u}_j}Z(\mathbf{u}_1,\mathbf{u}_j) - \frac{aU_{ex}(\mathbf{u}_j)}{k_BT} \qquad \text{(VIII.34)}$$

Here we have averaged over the φ angle of the $(j + 1)$st link and expanded a Boltzmann weighting factor containing the (weak) external field. In the limit we are considering $(\mathbf{u}_{j+1} - \mathbf{u}_j)^2 = (\pi - \theta_f)^2$; hence, if we put $ja = l$ we get the continuous version of eq VIII.34 using eq VIII.32 and VIII.33.

$$\frac{\partial Z(\mathbf{u}_1,\mathbf{u})}{\partial l} = (2P)^{-1}\Delta_{\mathbf{u}}Z(\mathbf{u}_1,\mathbf{u}) - \frac{U_{ex}(\mathbf{u})}{k_BT}Z(\mathbf{u}_1,\mathbf{u}) \qquad \text{(VIII.35)}$$

The boundary condition is $\lim_{l \to 0} Z(\mathbf{u}_1,\mathbf{u}) = \delta(\mathbf{u} - \mathbf{u}_1)$ so that Z is a Green function. Equation VIII.35 is an equation that has often been used in the polymer literature (see ref 38). It can be employed to illustrate the Khokhlov–Semenov approach,[29,30] an application of the Lifshitz theory.[39,40]

If the chain is long enough, the free energy must be extensive so that Z can be written in the form

$$Z(\mathbf{u}_1,\mathbf{u},L) \sim e^{-\mu_0 L}\psi(\mathbf{u}_1)\psi(\mathbf{u}) \qquad \text{(VIII.36)}$$

Alternatively, this may be viewed as the first term of an eigenfunction expansion.[39] We must get a product of independent factors because the probability factorizes for very large systems. Inserting eq VIII.36 into eq VIII.35 we obtain an eigenvalue equation

$$(2P)^{-1}\Delta\psi(\mathbf{u}) - \left(\frac{U_{ex}(\mathbf{u})}{k_BT} \right)\psi(\mathbf{u}) + \mu_0\psi(\mathbf{u}) = 0 \qquad \text{(VIII.37)}$$

There is no need to solve this equation. First, the eigenfunction $\psi(\mathbf{u})$ is simply connected to $f(\mathbf{u})$, the orientational distribution function we have been discussing all along. We just insert eq VIII.36 in eq VIII.28

$$f(\mathbf{u}) = \psi^2(\mathbf{u}) \qquad \text{(VIII.38)}$$

Second, we need the orientational entropy given by an expression like eq VIII.31 taking into account eq VIII.30

and VIII.36, neglecting end effects for the moment

$$\sigma = (\mathcal{F} - L\langle U_{ex}\rangle)/k_BT = \mu_0 L - \int_0^L ds \int du$$

$$f(\mathbf{u})\left(\frac{U_{ex}(\mathbf{u})}{k_BT}\right) = \int_0^L ds \int du\, f(\mathbf{u})\left(\mu_0 - \frac{U_{ex}(\mathbf{u})}{k_BT}\right)$$
$$(\text{VIII.39})$$

Thus, we can completely eliminate the eigenvalue μ_0 and the external field $U_{ex}(\mathbf{u})$ by using eq VIII.37

$$\sigma = -\frac{L}{2P}\int du\, f(\mathbf{u})\left(\frac{\Delta\psi(\mathbf{u})}{\psi(\mathbf{u})}\right) \qquad (\text{VIII.40})$$

This expression is conveniently rewritten in terms of the original variables with the help of eq VIII.38 and an integration by parts

$$\sigma = \frac{L}{8P}\int d\Omega\left(\frac{\partial f}{\partial\theta}\right)^2 f^{-1} \qquad (\text{VIII.41})$$

The Gaussian approximation eq II.14 yields

$$\sigma = L\alpha/(4P) = L/(4\lambda) \qquad (\text{VIII.42})$$

(e) Comparison. We reach the inescapable conclusion that the orientational free energy of a nematically confined wormlike polymer is proportional to α or $\langle\theta^2\rangle^{-1}$. The most general approach is that of the last section, which we might call the method of ground-state dominance. The external field (here caused by the excluded-volume effect) causes the spectrum of free energy levels to become partly discrete; i.e., a phase transition occurs. The state belonging to the eigenvalue μ_0 dominates. We need not go into the solution of the eigen equations, nor do we have to known μ_0. Equation VIII.41 along with say eq II.11 can be used directly for a variational principle for f. This is akin to the variational principle for the self-consistent field method in quantum mechanics.[41]

Starting equations like (VIII.19) but often using Maier–Saupe type potentials have appeared (e.g., refs 42–44). There is much value in a heuristic treatment along these lines. However, if we want a complete theory, even of the "mean-field" type, we would require a connection between the field U_{ex} in eq VIII.20 and the excluded-volume and other interactions. In general this connection is obscure. Anyway, if U_{ex} is nonstandard, solving Z becomes a complicated task. The merit of the Khokhlov–Semenov theory is to transpose all difficulties to a later stage. Finally, the internal consistency of equations like (VIII.20) may be suspect as pointed out by de Gennes[42] for the case of a stiff polymer dissolved in a simple nematic. The chain causes long-range perturbations within the ordered fluid so that Γ cannot be regarded as strictly constant. The Lifshitz theory appears to be able to circumvent all these difficulties.

In the method using the Helfrich theory of constrained fluctuations there are some assumptions in writing eq VIII.14 which could be weeded out if one were to consider using trial functions other than Gaussian. We have not yet considered such an extension of section b. Evidently this method is fast and elegant, its drawback being that it focuses on the second moments instead of the full distribution function. Of course, Helfrich derived his theory for steric interactions, which are difficult to take into account in any kind of treatment.

Finally, the scaling approach is simple and fastest, but any logarithmic terms that one can derive by devious means are suspect. The deflection length λ is a helpful length scale cropping up in these and other calculations. The maxim is to formulate λ and associate a free energy

k_BT with fluctuations on this length scale.

(f) Isotropic–Nematic Transition for Very Long Polymers. We now briefly review the isotropic–nematic phase transition in a solution of N long wormlike polymers.[28] When $P \gg D$ half the excluded volume, b_p, between two polymer chains of length L is essentially

$$b_p = \left(\frac{\pi}{4}\right)\left(\frac{L}{P}\right)^2 P^2D = \left(\frac{\pi}{4}\right)L^2D = \left(\frac{L}{P}\right)^2 b_m \qquad (\text{VIII.43})$$

This is not strictly true. First, we cannot just proceed as if each polymer were a collection of (L/P) persistence length fragments. Second, these fragments are not rigid. Corrections to eq VIII.43 have been calculated in part by Yamakawa and Stockmayer.[45] They may well need to be taken into account in the future but we shall use the approximation eq VIII.43 here. In accordance with this assumption eq II.12 also stands.

The Helmholtz free energy is now

$$\frac{\Delta F}{Nk_BT} = \frac{\mu^\circ}{k_BT} - 1 + \ln c_p' + \sigma(f) + b_p c_p'\rho(f) \qquad (\text{VIII.44})$$

with $\sigma = 0$ and $\rho = 1$ in the isotropic phase. It is convenient to rescale the polymer variables c_p' and b_p to quantities related to persistence segments $c_p' \equiv (Pc_m'/L)$ and $b_p \equiv (L/P)^2 b_m$. Since the orientational free energy is also extensive we can write $\sigma \equiv (L/P)\sigma_m$. Hence eq VIII.44 is reexpressed as

$$\frac{\Delta F}{Nk_BT} =$$
$$\frac{\mu^\circ}{k_BT} - 1 + \ln\left(\frac{P}{L}\right) + \ln c_m' + \left(\frac{L}{P}\right)\sigma_m + \left(\frac{L}{P}\right)b_m c_m'\rho \qquad (\text{VIII.45})$$

If eq II.13 is again our choice of trial function, we have from eq VIII.41

$$\sigma_m(\alpha) = \tfrac{1}{4}(\alpha - 1) + \mathcal{O}(e^{-2\alpha}) \qquad (\text{VIII.46})$$

Minimization of eq VIII.45 thus gives

$$c_a\rho_a'(\alpha) = -\tfrac{1}{4} \qquad (\text{VIII.47})$$

where $\rho_a'(\alpha)$ is given by eq II.26 and $c \equiv b_m c_m'$ from now on. For very long chains $(L/P \to \infty)$ we deduce the coexistence equations from eq VIII.45

$$2c_i = \tfrac{1}{4}(\alpha - 1) + 2c_a\rho_a \qquad (\text{VIII.48})$$

$$c_i^2 = c_a^2\rho_a \qquad (\text{VIII.49})$$

The numerical solution of eq VIII.47–49 is $c_i = 5.409$, $c_a = 6.197$, $\alpha = 6.502$, $\rho_a = 0.76185$, and order parameter $S = 1 - 3\alpha^{-1} + 3\alpha^{-2} = 0.610$. Note that we have to use the exact expression for ρ_a (eq II.26). If one uses only a few terms in the asymptotic expansion one regains the numerical results of Khokhlov and Semenov,[28] which are too low because α is not large enough (note also that their concentrations are scaled with respect to the Kuhn length). These results show that it is much harder to order stiff polymers because of their flexibility[28]—α shifts downward in comparison with the rigid-rod case whereas the coexistence number densities are enhanced. The width of the transition decreases. In addition, the stabilization free energy per persistence fragment is only $0.100k_BT$. A Gaussian theory has been outlined in ref 30. Its usefulness will be shown in the next section.

IX. End Effects and Bidispersity

(a) End Effects. The calculation of the previous section is valid for very long semiflexible polymers. Obviously

we also need a theory to account for the broad region between the fully rigid rod and very long coil limits. In this intermediate range of contour lengths it becomes impossible to assign only one orientational distribution function to the whole wormlike polymer.[29] Even when it is quite long, its ends are basically rodlike elements about a deflection length long. These elements are defects perturbing the behavior of the surrounding chains. At the other extreme a wormlike polymer of the order of a deflection length already has enough flexibility to modify the classical Onsager calculation. In addition, we must not forget to take into account the terms related to the energy of translation which were discarded in the analysis for very long polymers.

Unfortunately it is no mean task to derive the free energy of a nematic polymer for all contour lengths (but see section IXb). Khokhlov and Semenov[29] devised an elegant perturbation scheme, which is summarized below. They retained the logarithmic correction in eq VIII.39

$$\sigma = \frac{L}{8P} \int d\Omega \left(\frac{\partial f}{\partial \theta}\right)^2 f^{-1} - 2 \ln \left[\int f^{1/2} \, d\Omega\right] + \ln (4\pi) \qquad (L \gg P) \quad (IX.1)$$

(A term $\ln (4\pi)$ is included so that $\sigma = 0$ in the isotropic state.) By rearrangement of eq VIII.35 they also obtained the confinement entropy near the rod limit.[93]

$$\sigma = \int f \ln (4\pi f) \, d\Omega + \frac{L}{12P} \int d\Omega \left(\frac{\partial f}{\partial \theta}\right)^2 f^{-1} \qquad (L \ll P)$$
$$(IX.2)$$

Let us now calculate these expressions for the specific choice of the Onsager trial function

$$\sigma = \frac{L(\alpha - 1)}{4P} + \ln (\tfrac{1}{4}\alpha) \qquad (\alpha L \gg P) \quad (IX.3)$$

$$\sigma = \ln \alpha - 1 + \frac{L(\alpha - 1)}{6P} \qquad (\alpha L \ll P) \quad (IX.4)$$

Equation IX.3 shows that as expected there are end perturbations extending about a deflection length $\lambda = P/\alpha$ from both ends. The logarithmic term signifies the (roughly) rodlike nature of these defects. In a similar vein, slight bending fluctuations become a minor problem only when $L \lesssim \tfrac{1}{2}\lambda$.

Although we do not have the complete function $\sigma(L)$ (in the next section we do present the Gaussian approximation), we can still derive convenient expressions for the I–N transition variables by matching.[29] First, the perturbation terms in eq IX.3 and IX.4 are handled in the same manner as previously. If all units are scaled with respect to the persistence length, one obtains

$$N_P \equiv L/P \gg 1$$

$$c_i = 5.409 + 1.910 N_P^{-1}$$

$$c_a = 6.197 + 1.781 N_P^{-1} \qquad (IX.5)$$

$$S = 0.610 - 0.0948 N_P^{-1}$$

$$N_P \ll 1$$

$$c_i = 3.340 N_P^{-1} + 4.99$$

$$c_a = 4.486 N_P^{-1} - 1.458 \qquad (IX.6)$$

$$S = 0.847 - 1.487 N_P$$

The persistence length has been chosen as the reference scale because this is standard practice in wormlike chain theory. The Kuhn length is to be avoided because it no-

where enters the statistical formulation of the theory outlined here. The expressions (IX.5) and (IX.6) are modifications of those due to Khokhlov and Semenov.[29] The differences arise, apart from their scaling with the Kuhn length, because we have used the full expression for ρ (eq II.26) whereas Khokhlov and Semenov used only a couple of terms from the expansion of ρ. Of course, these modified Khokhlov–Semenov expressions are approximate; i.e., a full numerical analysis would be very useful because α is so low.

Next, we can combine formulas (IX.5) and (IX.6) by expressing them as ratios of polynomials[29]

$$c_i = \frac{3.34 + 5.97 N_P + 1.585 N_P^2}{N_P(1 + 0.293 N_P)} \qquad (IX.7a)$$

$$c_a = \frac{4.486 + 11.24 N_P + 17.54 N_P^2}{N_P(1 + 2.83 N_P)} \qquad (IX.7b)$$

It can be argued that such a procedure should work admirably:[29] the bifurcation density can be calculated in two ways, exactly and as above and the two calculations practically coincide. Still, it can be criticized (see discussion below eq IX.3). A detailed discussion of the original equations is presented in ref 29. The main conclusions are (i) the order parameter S has a minimum when the chain is about half a persistence length long, (ii) the transition width $(c_a - c_i)/c_i$ plunges to a very low value of 0.024 for the same contour length, and (iii) the length dependence of the transition is complicated and must be reckoned with when one assesses experiments.

(b) Bidispersity. If the influence of flexibility on the formation of the nematic phase for monodisperse polymers is pronounced, its effect on polydisperse systems can only be called startling. The original phase diagram for rods is completely changed. This will be seen from the calculations below, an extension of the theory of ref 21. They are preliminary and approximate but they provide hints of the complexity involved in trying to understand the phase behavior of real systems. Specifically, we will consider bidisperse semiflexible polymers of arbitrary contour lengths L_1 $(N_{P,1} = L_1/P)$ and L_2 $(N_{P,2} = L_2/P)$ with length ratio $q = L_2/L_1 \geq 1$. Instead of scaling quantities with respect to the persistence length, we shall use L_1. Thus the formalism is identical with that of section IV and all notation is the same. This also applies to the excluded-volume terms because the expressions for the covolume of rods are identical with those for stiff chains, at least to a first approximation as we have seen in section VIII. The only new terms are the orientational entropy ones.

The dominant terms in eq IX.3 and IX.4 come from the Gaussian part of the Onsager trial function. Fortunately, it is possible to calculate these leading terms exactly for all N_P from eq VIII.26. The total partition function is derived from eq VIII.30. As expected, the distribution according to eq VIII.28 is now not precisely a Gaussian. In order to get the leading terms, we simply focus on the averaged second moment $L^{-1} \int_0^L dl \, \langle \theta^2(l) \rangle$, which should equal $2\alpha^{-1}$, so that we again have a connection between Γ and α. The final result for the confinement entropy is given by

$$\sigma = \ln (\tfrac{1}{2}\alpha) + \ln [t^{-1} \sinh t(t \coth t + 1)] - t^2/(N_P\alpha)$$
$$(IX.8)$$

with

$$\Gamma N_P^2 \equiv t^2 = \tfrac{1}{2}\alpha N_P(t \coth t + 1)$$

For large α this function has the limiting behavior specified by eq IX.3 and IX.4 as it should.

We have found it convenient to replace eq IX.8 by the following highly accurate approximation which exhibits an explicit dependence on αN_P:

$$\sigma = \ln \alpha + \tfrac{1}{6}\alpha N_P + \tfrac{5}{12} \ln (\cosh (\tfrac{1}{5}\alpha N_P)) - \tfrac{19}{12} \ln 2 \tag{IX.9}$$

If we were to substitute $(\alpha - 1)N_P$ for αN_P in eq IX.9, the resulting σ might be reasonable for small α (say $\alpha \simeq 5$) even when N_P is of order unity. Phase diagrams calculated numerically with the help of this equation deviate significantly from eq IX.7 and IX.8 for intermediate N_P values. Thus, for monodisperse polymers a precise analysis should be given in the future. For now, we stick to the Gaussian approximation, which we also adopt for ρ_{jk}.

Minimizing the free energy (eq IV.5) and noting that x is still $N_2/N_1 + N_2$, $c_a = bc_a' = ((\pi/4)L_1{}^2D)NV^{-1}$, $q = N_{P,2}/N_{P,1}$, and $M_j \equiv \tfrac{1}{6}N_{P,1}(1 + \tfrac{1}{2} \tanh (\tfrac{1}{5} \alpha_j N_{P,j}))$, we get

$$\tfrac{1}{2}\pi^{-1/2}(M_1\alpha_1 + 1)\alpha_1{}^{1/2} = (1 - x_a + 2^{1/2}qhx_a)c_a \tag{IX.10}$$

$$\tfrac{1}{2}\pi^{-1/2}(M_2q\alpha_2 + 1)\alpha_2{}^{1/2} = q[qx_a + 2^{1/2}(1 - x_a)g]c_a \tag{IX.11}$$

As M_j goes to zero, we regain the equations of ref 21 described in section IV, whereas for very large M_j and $x_a = 0$ or $x_a = 1$ we recover the scaling theory of ref 30.

Equations IX.10 and IX.11 already allow us to assess the behavior of the nematic phase. We can easily distinguish several main regimes if we simply eliminate the concentration.

$$\frac{Q^{1/2}(M_2q\alpha_2 + 1)}{M_1\alpha_1 + 1} = \frac{q[qx_a + 2^{1/2}(1 - x_a)g]}{1 - x_a + 2^{1/2}x_aqh} \quad (\equiv W) \tag{IX.12}$$

(One can show that $Q \geqslant 1$: if $0 < x_a < 1$ the longer polymers are always more highly ordered.)

Region I: $q_2M_2\alpha_2 \ll 1$, **Rod–Rod Bidispersity (Section IV).**

Region II: $M_1\alpha_1 \ll 1$, $M_2q\alpha_2 \gg 1$, **Semiflexible Rod–Rigid Rod Case.** Equation IX.12 reduces to

$$M_2\alpha_2Q^{1/2} \simeq W \tag{IX.13}$$

For $x_aq \ll 1$ we have

$$Q \simeq (M_2\alpha_1)^{-1/2} \tag{IX.14}$$

Because of the requirement on α_2, $q(\alpha_1M_2)^{1/2} \gg 1$. When x_a is near unity

$$Q \simeq (M_2\alpha_1)^{-2/3} \tag{IX.15}$$

Again, we have the condition $q(\alpha_1M_2)^{1/3} \gg 1$.

Region III: $M_j\alpha_j \gg 1$, $M_1 \simeq M_2 = M = \tfrac{1}{4}N_{P,1}$, **Intermediately Long Bidisperse Polymers.** We write

$$\frac{Mq\alpha_2 + 1}{M\alpha_1 + 1} = qQ\left[1 - \left(\frac{qQ - 1}{qQ}\right)(M\alpha_1)^{-1}\right]$$

and expand eq IX.12 to first order in $(M\alpha_1)^{-1}$

$$Q - 1 = \frac{4}{7}\left(\frac{q - 1}{q}\right)(M\alpha_1)^{-1} \tag{IX.16}$$

Region IV: $Q \to 1$, **Very Long Polymers.**

In section IV we saw that Q depended on q in a complex fashion. Flexibility plays a role when the longer contour is about a deflection length or longer. Then Q is never large and is approximately independent of q. The basic reason for this is the extensivity of the free energy of a confined worm. The parameter η (eq IV.17) measuring the average excluded-volume effect in the nematic phase is readily derived for semiflexible polymers even if they are polydisperse. One just follows the same procedure as that of ref 24.

$$\eta = 2 + 2\sum_j M_jq_jx_{a,j}\alpha_j \tag{IX.17}$$

Here, $x_{a,j}$ is again the mole fraction of polymer of length q_jL_1 and L_1 is the contour length of the shortest polymer. Equation IX.17 shows that c_a is not slaved to c_i unless $M_{\max}$ is small enough. Therefore, the analysis of Odijk and Lekkerkerker[21] needs to be modified if further analytical progress is to be made. Anyway, the reentrant phenomenon is now highly unlikely.

X. Wormlike Polyelectrolytes

This section is a straightforward combination of the results outlined in sections VI and VIII. We now have to reckon with the ionic strength dependence of the persistence length but we leave this till later.

The derivation of the twisting effect is still valid provided the Debye radius never exceeds the deflection length. Thus, equations similar to (VI.9–11) still hold although they must be modified to account for the fact that when $h \to 0$ they should reduce to eq VIII.47–49 if the contour length is long enough. A perturbation analysis around the zero-order solution pertaining to the semiflexible polymer nematic is as straightforward as before

$$\delta c_i = 4.72h$$
$$\delta c_a = 4.97h \tag{X.1}$$
$$\delta \alpha = 0.53h$$

(As in section VI we could try writing $c_i \simeq 5.41(1 - 0.87h)^{-1}$ etc.)

In spite of the low zero-order value for α, the twisting effect is substantial, varying from about 10% to 100% if we extrapolate the numerical work of ref 22. The high concentrations at the phase transition are the cause of these nonnegligible increments. This essentially concludes our whole discussion of the isotropic–nematic transition for polymers and polyelectrolytes but let us close with some speculative remarks on salt-free polyelectrolytes.

Could intrinsically flexible polyelectrolytes ever form a nematic? Polyelectrolytes are now thought to be electrostatically stiffened by the charge groups along the backbone (see ref 46–50). The electrostatic persistence length P_e is proportional to the square of the Debye length κ^{-1} and can be quite a deal longer than the screening length itself. Hence the existence of a nematic phase appears plausible but it turns out that this feasibility depends very much on the precise values of several numerical coefficients as we shall now see.

The screening should be as weak as possible so we consider solutions without added electrolyte. Furthermore we choose a polyelectrolyte that is not too strong; the distance A_s between charges along the contour is smaller than or equal to the Bjerrum length $Q_B = e^2/k_BTD_0$ (with $D_0 = $ electrical permittivity of solvent) so that the Debye–Hückel approximation is not bad. The Debye length κ^{-1} is given by

$$\kappa^2 = 4\pi Q_Bc_A \tag{X.2}$$

where c_A is the number density of charges in solution coming from the dissociation of the dissolved polyelectrolyte molecules. If the polyelectrolyte chains are intrinsically very flexible, we can disregard the structural persistence length and write for P^{46-48}

$$P \simeq P_e = \Gamma_1 Q_B / (4 A_s^2 \kappa^2) \qquad (\text{X.3})$$

where Γ_i are slowly varying functions of order unity to be discussed below. Finally, we need the effective diameter of the chains.[22,27]

$$D_{eff} = \kappa^{-1} \left(\ln \left(\frac{4\pi Q_B \Gamma_2}{A_s^2 \kappa} \right) + C_E - \frac{1}{2} \right) \qquad (\text{X.4})$$

According to sections VI and VIII the condition for the formation of a nematic is simply

$$\Gamma_1 (64 A_s \kappa)^{-1} \left[\ln \left(\frac{4\pi Q_B \Gamma_2}{A_s^2 \kappa} \right) + C_E - \frac{1}{2} \right] > \Gamma_3 c_i \qquad (\text{X.5})$$

together with

$$P_e D_{eff}^{-1} > \Gamma_4 \qquad (\text{X.6})$$

We note the following:

(1) If all the Γ_i except Γ_4 are set equal to unity, the smallest value of Debye radius κ_0^{-1} is obtained from eq X.5 when $A_s = Q_B$: $\kappa_0^{-1} \simeq 380$ Å ($Q_B = 7.14$ Å for H_2O at 25 °C and $c_i \simeq 5.4$).

(2) Γ_3 could be as large as 1.5 because of the twisting effect ($h \rightarrow (D_{eff}\kappa)^{-1}$ as $D \rightarrow 0$) and end effects perturbing the limit of infinite contour length, both of these perturbations having been described earlier. Γ_2 is slightly smaller than unity because of nonlinear screening in the Poisson–Boltzmann equation describing the outer double layers of interacting polyions.

(3) Numerical work has shown that $\Gamma_1 < 1$.[51,52] Furthermore, end effects can be drastic[53,54] so that Γ_1 can easily be as low as 0.5 even for very long polyelectrolytes at low ionic strengths. Thus in order to satisfy requirement (X.5) κ^{-1} should be at least around 1000 Å. The persistence length would then be about 36 000 Å, which should be compared with the effective diameter of about 7500 Å. The ratio P/D_{eff} ought to be very large if eq X.5 is to remain useful; it is only about 4, enough to cause the transition if one extrapolates recent Monte Carlo work[55,56] but eq X.5 is of course suspect in that case. We must conclude that there is a definite theoretical possibility of an anisotropic phase for salt-free solutions of polyelectrolytes that are intrinsically flexible although a very precise analysis could conceivably yield the opposite conclusion. Anyway, in terms of experimental quantities we need concentrations as low as 0.01 g/L and molecular weights as high as a few million. Reasonably accurate measurements at these concentrations are feasible nowadays.[57] Measuring very low birefringences ($\Delta n \simeq 10^{-9}$) has also become fairly standard.[58] Thus, the problem is not academic.

XI. Comparison with Experiments

It is out of the question that we can probe ideally rodlike behavior for semiflexible polymers of normal stiffness. On the one hand, we must have contour lengths at least 20 times longer than the diameter in order to avoid worrisome end effects and higher virial coefficients in the theory; on the other hand, the contour length should definitely not exceed the deflection length. Near the rod limit typical values of α are about 15 so that we have $P \gtrsim 300D$ as a minimum requirement. This condition is fulfilled for the extremely stiff biopolymers muscle filament and fd virus, the persistence lengths of which (of the order of 10^4 Å) have been measured via dynamic light scattering.[59,60] Thus, for the usual stiff polymers we are forced to take the semiflexibility effect into account, and so we need to know the persistence length quite accurately.

Table III
Ratio X of the Experimental Number Density $c_{i,e}$ to the Theoretical One of Eq IX.7 as a Function of the Number of Persistence Lengths N_P

polymer	N_P	$c_{i,e}$	X	$\varphi_i L/D$
schizophyllan[a]	0.171	1.57	0.64	2.68
	0.342	11.9	0.81	4.08
	1.25	6.6	0.84	8.2
	2.08	5.7	0.85	11.9
PBLG[b]	0.428	10.8	1.19	4.61
	1.28	8.6	1.11	11.0
	2.53	7.4	1.15	18.8
DNA[c]	1.05	6.4	0.78	6.7
	1	8.5	0.85	8.5
	1.59	5.7	0.70	9.1
	2.97	4.4	0.61	13.1

[a] Reference 67 except $N_P = 1.25$ (ref 64); solvent H_2O. The persistence length is taken to be 1800 Å, and the diameter 16.7 Å. [b] Reference 71 except $N_P = 1.05$ (ref 72); solvent dioxane with 4% TFA except $N_P = 1.05$ (DMF). Persistence length is taken to be 800 Å, and the diameter 15.5 Å. [c] Reference 84; solvent 0.102 N aqueous buffer solution. The persistence length was assumed to be 500 Å and the effective diameter and twisting parameter were calculated from ref 22. Ions from the DNA were accounted for via the condensation picture. The helix diameter was taken to be 20 Å.

As is well-known the determination of the persistence length is not an easy task. Only by using a number of disparate techniques is it possible to give an estimate in which one can have some confidence. Furthermore, because we do not want to stray too far from the validity of the second virial approximation, the choice of systems to test the theories reviewed here is narrowed down to a very small number.

We first consider relatively monodisperse aqueous solutions of the interesting polysaccharide schizophyllan, which has been exhaustively and carefully analyzed during the past few years.[61-70] Although the triple helix is not very thick ($D_h \simeq 30$ Å) it is remarkably stiff (estimates of P vary from 1300 to 2000 Å[61-63,70]). Van, Itou, and Teramoto[64,65,67] have obtained the isotropic–anisotropic phase diagram for molecular weights that are in a range broad enough to test the influence of semiflexibility. Although the anisotropic phase is cholesteric we will assume for the moment that the influence of interactions other than steric are negligible. Assuming $P = 1800$ Å and $D = 16.7$ Å as a reasonable value for the effective diameter,[64,65,67] we have tabulated the quantity $X = c_{i,e}/c_i = \varphi_{i,e}(P/D)c_i^{-1}$ with the volume fraction $\varphi_{i,e}$ given by $[1 + (w^{-1} - 1)(V_0/V_P)]$, with w the weight fraction and $V_0/V_P = 1.616$ the ratio of the specific volumes of H_2O and schizophyllan and c_i given by eq IX.7 (see Table III). In view of the uncertainty in P and D the theory is in reasonably good agreement. Note that the volume fraction scaled with respect to contour length varies by a factor of more than 4: a rodlike model fails although the dilute solution behavior for the first two samples would be described well by rod models. The first two entries can be used to estimate the persistence length from eq X.6. It would be about 2200 Å, in good agreement with, say, that estimated from viscosity data.[62]

Next we have tabulated some results on poly(γ-benzyl L-glutamate) due to Fernandes and Du Pré[3,71] along with those of Sakamoto[72] for comparison. This polypeptide is less stiff than schizophyllan but stiff enough for our purpose. We have taken a persistence length of 800 Å (lower and higher values have been given[73-77]) and assumed D is the diameter of the helix (15.5 Å). The modified Khokhlov–Semenov expression is again quite reasonable: X is constant and close to unity. The result given by Sakamoto shows the difficulty in interpreting c_i (he also dis-

Table IV
Values of c_a, α_1, α_2, and Q Calculated from Eq IX.10, IX.11, and IX.17 Using the Experimental Values $\Pi_{i,e}$ and $x_{a,e}$ As Derived from the Experimental Data for Bidisperse Schizophyllan[67] according to the Text

q	$\Pi_{i,e}$	$x_{a,e}$	$c_{a,e}$	c_a	α_1	α_2	Q	$\langle\alpha\rangle_w{}^b$	$C_{a,rod}{}^a$
6.06	8.87	0.300	1.419	1.272	6.9	10.6	1.54	8.1	2.96
6.06	15.57	0.429	1.261	1.51	10.4	14.4	1.38	18.4	5.19
6.06	23.8	0.114	3.75	3.65	12.1	16.2	1.34	13.3	7.92
6.06	26.2	0.0614	4.57	4.51	12.3	16.3	1.33	13.0	8.72
6.06	24.6	0.0307	4.95	4.77	11.4	15.4	1.35	10.6	8.18
6.06	25.9	0.0106	5.37	5.29	11.4	15.4	1.35	10.8	8.63
12.2	3.34	0.478	0.322	0.340	5.8	13.4	2.32	14.6	1.113
12.2	7.17	0.304	0.845	0.772	10.2	18.5	1.85	15.7	2.39
12.2	13.13	0.118	1.97	1.99	14.0	22.6	1.63	20.0	4.37

^{a} For comparison the number density $c_{a,rod}$ calculated as if the polymers had infinite stiffness is also shown. ^{b} The experimental $\langle\alpha\rangle_w$ is calculated using $\bar{M} \simeq 0.08$ for $q = 12.2$ and $\bar{M} \simeq 0.04$ for $q = 6.06$.

Table V
Theoretical Values of c_a, α_1, and Q Calculated via Eq IX.10, IX.11, and IX.17 from the Experimental Values^a of $\Pi_{i,e}$ and $x_{a,1}$ or $x_{a,2}$ Derived from Ref 67

$\Pi_{i,e}$	$x_{a,2}$	$c_{a,2}$	c_a	α_1	Q	$x_{a,1}$	$c_{a,1}$	c_a	α_1	Q
14.37	0.00349	3.73	3.80	10.8	1.74	0.0707	2.61	2.61	14.0	1.61
16.26	0.00167	4.01	4.22	12.0	1.68	0.0822	2.46	2.68	15.6	1.56
15.03	0.00167	4.02	3.98	11.1	1.72	0.0388	3.50	3.16	13.3	1.63
29.2	0.00116	4.53	6.56	19.4	1.45	0.1268	2.32	3.25	23.9	1.39

^{a} 1 = first anisotropic phase, and extension of the phase of Table IV; 2 = second cholesteric phase.

cussed the influence of solvent power in his paper; moreover, association is asserted to happen sometimes). Slight adjustment of P and D could possibly bring the data in line.

It is very hard to find data suitable within our context on polyelectrolytes. The beautiful work on tobacco mosaic virus[78-83] cannot be analyzed at present because the axial ratio $L/\tilde{D}$ is only of order 10. Recent measurements[84] by Rill et al. on DNA are only slightly more convenient, $L/\tilde{D}$ being about 12. In Table III these results are compared with the polyelectrolyte theory (sections VI and X): P is about 500 Å, $\tilde{D}$ is about 40 Å (corrected also for the presence of small ions from the DNA itself), and h is about 0.15. Because adjusting P upward would deviate from the consensus on the magnitude of this quantity and decreasing $\tilde{D}$ would not make the quantity X constant, we conclude that the theory does not work (at an ionic strength of 0.1 M). The virial expansion must be taken to higher order. Brian et al.[85] and Trohalaki et al.[86] have discussed the use of scaled particle theory although the semiflexibility effect definitely plays a larger role.

Itou and Teramoto[65,67] have studied coexistence diagrams of two bidisperse mixtures of schizophyllan, the samples being the same as those of Table III. We compare the analytical expression for the osmotic pressure developed in section IX with their measurements as follows (see Table IV). From their values of the weight fraction w and weight ratio ξ_1 of the polymer of smaller contour length to the total amount of polymer we calculate the mole fraction $x = (1 - \xi_1)(1 + (q - 1)\xi_1)^{-1}$ and scaled number density $c = (L_1/D)[\xi_1 + q^{-1}(1 - \xi_1)]/[1 + (w^{-1} - 1)(V_0/V_P)]$. Equation IV.9 gives the scaled osmotic pressure $\Pi_{i,e}$ in the isotropic phase while c_a is then derived from eq IX.10, IX.11, and IX.17 using the empirical $x_{a,e}$ and q values. The agreement is good. We have also shown the entirely reasonable values of α_1, α_2, and Q that come out of the equations. Also tabulated is the empirical quantity

$$\langle\alpha\rangle_w = \frac{\Pi_{i,e} - 3c_{a,e}}{2\bar{M}(1 - x_{a,e} + x_{a,e}q)}$$

This should equal $\alpha_1(1 - x_{a,e}) + x_{a,e}q\alpha_2$ via eq IX.17 and so $\alpha_1 \lesssim \langle\alpha\rangle_w \lesssim \alpha_2$. As one can see this inequality is almost always satisfied, $\langle\alpha\rangle_w$ being close to the theoretical value

α_1 when $x_{a,e}$ is small and near α_2 when $x_{a,e}q$ approaches unity. Thus, $\langle\alpha\rangle_w$ apparently gives an indication of the degree of orientational order in a system of bidisperse semiflexible polymers. Note that eq IX.17 shows that a similar expression holds for polydisperse systems. A last remark concerns the sensitivity of c_a to the chosen value of $N_{P,1}$. An increase of 10% in $N_{P,1}$ causes a decrease of about 1.5% in c_a on the average. Because of the uncertainties in P, M_j could be off by a factor of 1.5 or more. Thus, the average discrepancy of about 5% between c_a and $c_{a,e}$ can easily be rationalized. If we were to assume the polymers were rods ($M_j = 0$), the measurements would be unexplainable (see last column of Table IV).

Next, in Table V we consider the data[65,67] of Itou and Teramoto for higher concentrations where another anisotropic phase appears (A_2). The concentrations $c_{a,e}$ in both cholesteric phases (A_1 and A_2) are still remarkably well predicted. However, as expected the A_2 phase is unstable within an athermal context: ΔF_a is about $0.3k_BT$ per persistence fragment higher than ΔF_i (the A_1 phase is always very stable). Thus, weak attractive forces could easily stabilize the A_2 phase although they would only mildly perturb the osmotic pressure itself, in this way explaining why the athermal model can rationalize the $c_{a,e}$ values.

XII. Concluding Remarks

Our preliminary comparison of experimental results on very stiff polymers with the (slightly amended) Khokhlov–Semenov theory[28,29] and the extensions developed here of the work of Odijk and Lekkerkerker[21] shows that the virial approach is a good approximate way of describing the formation of the nematic phase. The effect of semiflexibility, independently introduced by several authors within different contexts, is very large: the experimental work outlined in Tables III and IV cannot be explained by appealing to fully rigid models.

The scope of this review has been restricted to a small number of topics. We have not dealt with important subjects like anisotropic micelles, elastic constants, or nematodynamics, but the author hopes to address these in future contributions.[99] This paper has been concerned with applications of the Onsager approach. There are a myriad other approaches but in these, detailed calculations

for realistic polymer systems have lagged behind those outlined here. We have also neglected to include van der Waals forces. This has been attempted by Grosberg and Khokhlov,[4] although very approximately, and this work will have to be reanalyzed in the future.

A last remark concerns the (slight) confusion about the concentration dependence of the persistence length in the nematic phase. For intrinsically stiff polymers the persistence length is a constant quantity in all expressions reviewed here. This can be easily seen from the derivations—we either need the local resistance to bending of the probe polymer, or we do not need the persistence length at all as in establishing the excluded-volume effect. In a number of papers the global persistence length has been discussed[42,43,87-91] i.e., a length scale connected with the average dimension of one chain. In our case this scale increases with higher nematic concentrations as calculated in detail by Khokhlov and Semenov.[87] But a locally defined scale like the deflection length decreases. This simply means the nematic field has more grip on the polymer chain so that it is more difficult to fold, in turn implying that the global persistence length is enhanced. There is no paradox. In fact, it is a simple exercise in scaling to get one length scale from the other.

Acknowledgment. The author thanks Dr. M. Frissen and Prof. H. N. W. Lekkerkerker for discussions.

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(92) Here, we have used the fact that in the limit $L\lambda^{-1} \rightarrow \infty$ the total free energy $\mathcal{F} = -k_BT \ln Z_{tot}$ is asymptotically equal to $\langle \Delta F \rangle$ even though the latter must be viewed as merely an averaged "Hamiltonian". The difference is an end effect, not an extensive quantity. The derivative of eq IX.9 shows that for finite polymers $\langle U_{ex} \rangle \neq \langle \Delta F_b \rangle$ and $\langle \Delta F \rangle \neq \mathcal{F}$.
(93) Equation IX.2 is derived as follows. In eq VIII.35 the term containing the Laplacian is regarded as a perturbation so that

one first solves eq VIII.35 to zero order (i.e., for a rod). Regular perturbation theory gives the first-order term expressing deviations from the rigid rod configuration (one must also retain terms of order contour length squared). Next we get the distribution $f(\theta)$ from eq VIII.28 and the expression $\sigma k_B T = \mathscr{F} - \langle U_{ex} \rangle$ is rewritten in terms of this f by the use of the identity $\langle \Delta U_{ex} \rangle = {}^1\!/_2 N_P \langle (\nabla U_{ex})^2 \rangle$ obtained by integrating by parts. It is interesting to note that this scheme is regular even though all quantities are singular; one would usually resort to a WKB approximation.

(94) The free energy difference per rod $(\Delta F_i - \Delta F_a)/N$ is much smaller than $k_B T$ so in this sense the first-order transition can be considered weak. However, from this viewpoint the order parameter and difference in densities are then anomalously large. Compare with the discussions in ref 14 and 23.

(95) The mechanism of the electrostatic twisting force is exhaustively reviewed and analyzed in ref 22. A scaling argument may help in understanding the form of eq VI.1. Consider two line charges skewed at an angle γ and separated by more than a screening distance κ^{-1} so that the outer double layers can be treated in the Debye–Hückel approximation. The cross section of the two overlapping double layers can be seen to be of order $\kappa^{-2} \sin^{-1} \gamma$. If the effective linear charge density is ν charges per unit length, we have

$$w(x \simeq \kappa^{-1}) \sim \nu^2 / (\kappa \sin \gamma)$$

This must be multiplied by a screening factor in order to arrive at eq V.1.

(96) Some numerical work has also been published recently by: Lee, S. D.; Meyer, R. B. *J. Chem. Phys.* **1986**, *84*, 3443. For comments, see ref 22.

(97) McMullen, W. E.; Gelbart, W. M.; Ben-Shaul, A. *J. Chem. Phys.* **1985**, *82*, 5616. These authors use a Legendre expansion to only second order which gives qualitative results (see ref 20). In this review we discuss expansions appropriate to highly ordered nematics.

(98) Some of these (qualitative) conclusions were first reached by Frost and Flory (Frost, R. S.; Flory, P. J. *Macromolecules* **1978**, *11*, 1134) within the Flory approximation.

(99) The approaches outlined in this review are applied to calculations of the elastic moduli in Odijk (Odijk, T. *Liq. Cryst.*, in press) and to micellar solutions in Odijk (Odijk, T. *J. Phys. (Les Ulis, Fr.)*, in press).

Articles

A Statistical Thermodynamic Theory of Thermotropic Linear Main-Chain Polymeric Liquid Crystals

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ABSTRACT: A statistical thermodynamic theory of thermotropic, main-chain polymeric liquid crystalline melts is developed by application and extension of a previously formulated statistical mechanical theory of rigid rod fluids (Boehm, R. E.; Martire, D. E. *Mol. Phys.* **1978**, *36*, 1). Each polymer molecule consists of M monomeric units bonded contiguously along a chain, and each monomeric unit in the isotropic melt consists of a rigid mesogenic core of $r + 1$ consecutive segments followed by t contiguous flexible segments. A free energy density is formulated that includes both short-range packing contributions and long-range anisotropic and isotropic dispersion energy contributions. Ordering of the mesogenic cores in the nematic melt is assumed to generate an environmentally induced tension that acts along the backbone of each chain and increases the average end-to-end chain length along the preferred direction, and an extension or enhanced ordering of the spacer groups in each monomer results. The enhanced ordering of the spacer groups leads to predictions of somewhat larger order parameters, transition entropies, and transition enthalpies than those typically observed for low molecular weight nematogens. Also under certain conditions an additional highly anisotropic mesophase is predicted to appear, in agreement with the results of Vasilenko et al. (Vasilenko, S. V.; Khokhlov, A. R.; Shibaev, V. P. *Macromolecules* **1984**, *17*, 2270). The thermodynamic properties of (hypothetical) homologous series of linear mesogenic polymers formed by increasing t for fixed r and M are also calculated and predict the experimentally observed trends of decreasing transition temperature and increasing transition entropy and enthalpy with increasing t. A possible mechanism for inclusion of odd–even variations in the thermodynamic properties is also discussed. The dependence of the statistical thermodynamic properties on M is also determined, and the results appear to be consistent for the most part with the experimental trends.

I. Introduction

Liquid crystalline polymers which have their mesogenic elements separated by flexible or semiflexible spacer groups such as $-(CH_2)_n-$, $-[Si(CH_3)_2O]_n-$, or $-(CH_2CH_2O)_n-$ often exhibit thermotropic mesophases with moderate anisotropic–isotropic phase transition temperatures considerably below that required for thermal degradation of the macromolecule. Several different linear nematic, smectic, and cholesteric polymers with moderate transition temperatures have been synthesized by condensation of mesogenic diols, diphenols, or diacid chlorides with flexible diols, silanols, or diacid chlorides.[1] The thermodynamic and structural properties have also been measured for a variety of linear polymeric liquid crystals. For example, Blumstein and Thomas (BT)[2] have measured the thermodynamic transition properties of a homologous series of mesogenic, thermotropic polyesters derived from 4,4′-dihydroxy-2,2′-dimethylazoxybenzene and alkanedioic acids having from $n = 2$ to $n = 14$ methylene groups which exhibit isotropic–nematic transitions for $n > 2$ at moderate temperatures (255 to 120 °C). Krigbaum, Watanabe, and Ishikawa[3] (KWI) have investigated the thermodynamic and structural properties of the mesophases of thermotropic polyesters synthesized from 4,4′-dihydroxybiphenyl