

ASPECTS OF THE EQUILIBRIUM THEORY OF LYOTROPIC POLYMER LIQUID CRYSTALS

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LYOTROPIC POLYMER LIQUID CRYSTALS**

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PROEFSCHRIFT

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus,
prof.drs. P.A. Schenck,
in het openbaar te verdedigen
ten overstaan van een commissie
aangewezen door het College van Dekanen
op 26 januari 1989 te 16.00 uur door

Gerard Jan Vroege

doctorandus in de scheikunde
geboren te Beverwijk



krips repro meppel

**TR diss
1697**

Dit proefschrift is goedgekeurd door de promotor

prof.dr. T. Odijk

STELLINGEN

1. De afleiding die Taratuta et al. geven van de uitdrukking voor de "buig" elastische constante van nematische polymeren maakt gebruik van een macroscopische beschrijving op moleculair niveau en laat daarmee ten onrechte de statistische mechanica buiten beschouwing.

V.G.Taratuta, F.Lonberg & R.B.Meyer, Phys.Rev.A 37, 1831 (1988)

2. De reden waarom Vertogen en de Jeu de Onsagertheorie van vloeibare kristallen ook in de dunne staaflimiet als kwalitatief kenschetsen is uitsluitend het gevolg van de benaderingen in hun eigen afleiding. Dit is derhalve een wetenschappelijke blunder.

G.Vertogen & W.H.de Jeu, Thermotropic Liquid Crystals, Fundamentals (Springer, Berlin, 1988)

3. Het artikel van Colot et al. suggereert dat een Maier-Saupe type distributiefunctie een goede benadering is voor de oplossing van de Onsagertheorie van nematische staven. Dit is onjuist.

J.-L.Colot, X.-G.Wu, H.Xu & M.Baus, Phys.Rev.A 38, 2022 (1988)

4. Het is merkwaardig dat Thirumalai weliswaar Fesjian bedankt voor het geven van enkele bruikbare referenties maar dat daarbij de belangrijkste referentie (namelijk die naar Khokhlov en Semenov) niet doorgekomen is.

D.Thirumalai, J.Chem.Phys. 84, 5869 (1986)

S.Fesjian & H.L.Frisch, J.Chem.Phys. 80, 4410 (1984)

A.R.Khokhlov & A.N.Semenov, Macromolecules 15, 1272 (1982)

5. De door Fixman gegeven uitdrukking voor het geïnduceerde dipoolmoment van een geladen staaf in de dunne dubbellaagbenadering valt relatief eenvoudig uit te breiden tot geladen ketens.

M.Fixman, Macromolecules 13, 711 (1980)

6. De uitdrukking voor de globale persistentielengte van lange wormachtige ketens in termen van de oriëntatie-distributiefunctie (zoals gegeven in dit proefschrift) is ook geldig voor willekeurige interacties, mits die beschreven kunnen worden met behulp van een "gemiddeld veld" met een nematische symmetrie.

Formules (IV.8.3) en (IV.8.13) van dit proefschrift

7. Formule (V.A.2) van dit proefschrift is van toepassing op staven indien de factor 2 in de noemer vervangen wordt door $(2 + 1/c_{i,0})$.
8. Bij uitvoering van het reorganisatieplan (oktober 1988) voor de Faculteit der Scheikundige Technologie en Materiaalkunde maakt de Technische Universiteit Delft de aanduiding Universiteit ongeloofwaardig.
9. Het is betreurenswaardig dat Mstislav Rostropovich zich de laatste jaren steeds meer toelegt op dirigeren.
10. De kosten van de twee wildviaducten over de A50 in verhouding tot die van de aanleg van de weg zelf kunnen in het licht van de totale uitgaven van de overheid voor natuurbehoud slechts gezien worden als een gigantische afkoopsom.

Delft, 26 januari 1989

G.J. Vroege

Aan Ronald
en mijn ouders

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CHAPTER I

GENERAL INTRODUCTION

In this chapter we give a brief introduction to liquid crystals and in particular to polymer liquid crystals. We also sketch the so-called virial theories for polymer liquid crystals which form the theoretical basis of this thesis and discuss the experiments available within this context. As we must necessarily be very concise it may be helpful to give some references to standard texts. For low molecular weight liquid crystals these are for instance the books by de Gennes [1] and Chandrasekhar [2] and a review by Stephen and Straley [3], for polymer liquid crystals we can recommend the book by Ciferri et al. [4], while there are several review articles [5-8]. Finally, the virial theories are extensively reviewed in a recent paper by Odijk [9] and some earlier papers [10-12].

I.1 Liquid Crystals

A liquid crystal phase consists of molecules which are *orientationally* ordered, whereas long-range *positional* order (which occurs in a true crystal) is either totally absent or only present in one or two dimensions. The constituent molecules of these liquid crystals are anisometric (which means that their extension in one dimension is markedly different from those in the other two dimensions as for rodlike or platelike particles) and can be both of low molecular weight or macromolecular in character. Before we discuss some possible different phases and properties, it is important to stress that for entropic reasons even the orientational order is not perfect in a liquid crystal: the molecules form a more or less narrow angular distribution around the average direction, the so-called director ($\mathbf{n}$).

We now give a short description of the most important phases:

- a) The *nematic* phase is the simplest type, where the molecules are directed more or less parallel but do not show any long-range positional order (see fig. 1a). In general a nematic phase is uniaxial: it exhibits cylindrical symmetry around the director as well as an inversion symmetry. In this thesis we will be involved mainly with these uniaxial nematic phases.
- b) The *cholesteric* phase consists of chiral molecules (which are not identical with their mirror images). Locally it closely resembles the nematic phase. However, on a larger length scale the very small chiral interactions collectively tend to gradually rotate the director throughout space (see fig. 1b). The pitch of this rotation is often on the order of the wavelength of visible light, which results in selective reflection and colored samples.
- c) There is a host of liquid crystalline phases showing partial positional order apart from orientational order. For example in the *smectic A* phase (fig. 1c)

the molecules are orderly arranged in layers (like in a crystal) but have a random distribution of their centers of mass within each layer (like in a liquid). In the smectic A case the molecules are on average directed perpendicular to the layers, while in the similar smectic C the molecules are tilted.

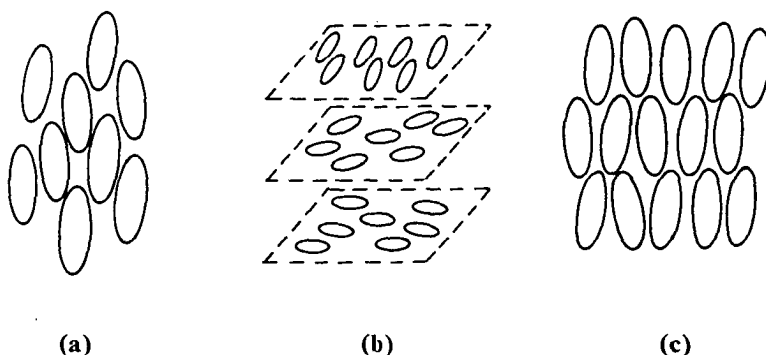


Fig. 1 Location of molecules in the liquid crystalline state (a) nematic phase (b) three sections through a cholesteric phase (c) smectic A phase (side view)

When heated, some low molecular compounds of sufficient anisotropy show one or more liquid crystalline phases between the crystalline and the liquid phase. Generally, these phases exhibit less order with increasing temperature, undergoing phase transitions at well-defined temperatures. As an example we mention 4,4'-di-heptyloxyazoxybenzene (see fig. 2) with the following phases [13]

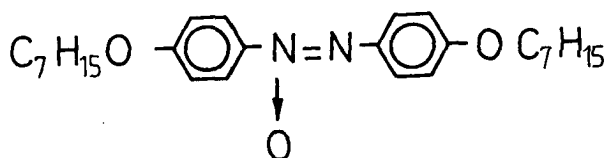
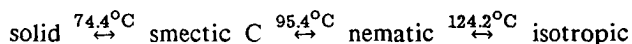


Fig. 2 4,4'-di-heptyloxyazoxybenzene

Because of the partial ordering present in liquid crystals, they possess quite peculiar properties. First of all liquid crystals are anisotropic because of

the orientational ordering, which is reflected in birefringence and polarization of transmitted or reflected light. Secondly, the anisometric form of the constituent molecules also means that they can be easily oriented by external fields (such as electric, magnetic or flow fields). These basic features explain the widespread use of liquid crystals in optical displays.

The position of liquid crystals in between true liquids and true crystals also turns up in their visco-elastic properties. On the one hand they are able to transmit special types of distortion (viz. those involving a static torque) like a solid because of their partial ordering, on the other hand they can flow like a liquid. We shall discuss this topic for nematics. To that purpose it is useful to have a closer look at the director field $\mathbf{n}$. This vector field describes the average direction of the molecules at each point of space, averaged over a volume element large enough to contain many molecules but yet small enough to determine a local value. Note that in a nematic the director is not an ordinary vector, since $-\mathbf{n}$ describes the same state as a result of the inversion symmetry. To describe the degree of ordering around the director it is common to use the order parameter

$$S \equiv \langle P_2(\cos\theta) \rangle = \left\langle \frac{3\cos^2\theta - 1}{2} \right\rangle \quad (\text{I.1.1})$$

where θ is the angle between a molecule and the director, the pointed brackets indicate an ensemble average and $P_2(\cos\theta)$ is the second order Legendre polynomial. S takes the value 1 for perfectly ordered molecules and the value 0 for randomly oriented molecules (in principle $-1/2$ is the lowest value S can take, viz. when all molecules would lie perpendicular to the director). The director field does not have to be uniform in space and it has in fact turned out to be very useful to describe the multi-domain structure and defects [1-3,14] (fig. 3), which usually occur in a liquid crystal when prepared without taking special precautions.

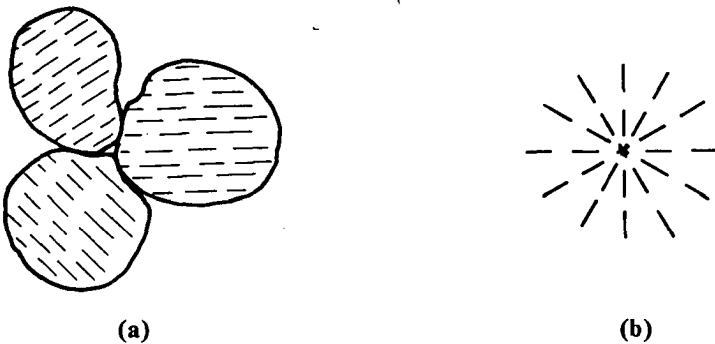


Fig. 3 (a) Multi-domain structure: every domain has its own director
(b) Defect in the director pattern

The concept of the director field has also been applied in describing the elastic deformations classified by Frank [15] in three fundamental types (see fig. 4). The total elastic energy is given by the energy density [1,3]

$$\frac{\Delta F_d}{V} = \frac{1}{2}K_1|\nabla\cdot\mathbf{n}|^2 + \frac{1}{2}K_2|\mathbf{n}\cdot\nabla\times\mathbf{n}|^2 + \frac{1}{2}K_3|\mathbf{n}\times\nabla\times\mathbf{n}|^2 \quad (\text{I.1.2})$$

integrated over the sample. K_1 , K_2 and K_3 are the elastic constants associated with each type of distortion. We recognize the usual form of an elastic energy: 1/2 times an elastic constant times the distortion squared. The source of elasticity in nematics is therefore the distortion of the director field against which the liquid crystal offers resistance. The energy involved in this process is generally very low. Contrary to the above, the effects occurring in a flowing nematic are of a dynamic character. Because of the complicated coupling between the velocity field and the director field a single viscosity is not sufficient to describe these dynamic effects [1-3]: it is necessary to introduce 5 different viscosities to describe a general flow in a nematic. A way to determine both elastic constants and viscosities is dynamic light scattering where the scattering is caused by fluctuations in the director field, in which both flow and elasticity are involved [1-3,16]. Another way to obtain the elastic constants is to measure the critical external field (e.g. a magnetic) which induces the respective director distortions [1-3,16].

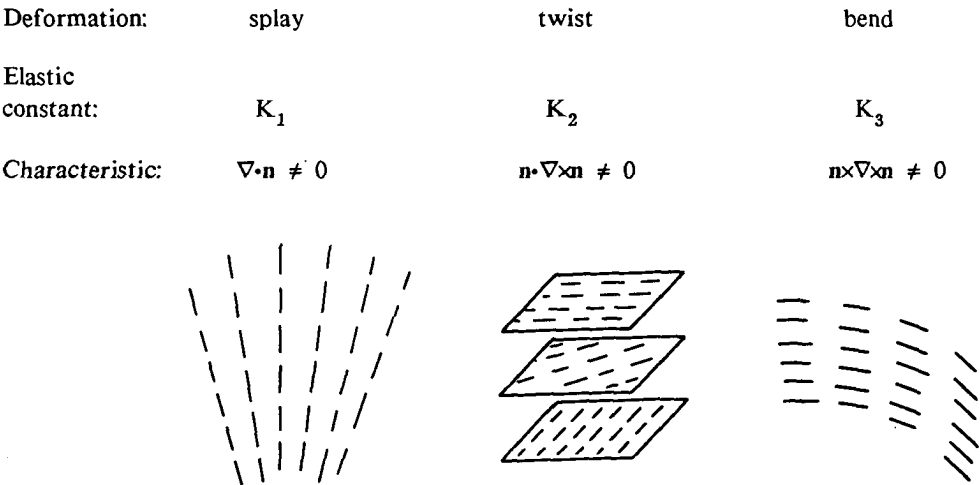


Fig. 4 The three fundamental deformations of a nematic liquid crystal

1.2 Polymer Liquid Crystals

One way to obtain liquid crystals from polymers is to attach (a) polymerizable group(s) to the small rigid molecule and build a macromolecule from it. Depending on the configuration we can distinguish two groups of liquid crystal polymers (LCP's):

a) *Main-chain* LCP's [17,18]: the rigid units are part of the polymer chain (fig. 5a)

b) *Side-chain* LCP's [19-21]: the rigid units are attached to the (flexible) polymer chain (fig. 5b)

Like low molecular weight liquid crystals the polymer liquid crystals thus formed are often *thermotropic*, i.e., they undergo a phase transition as a function of temperature. Because the melting temperature of these materials sometimes gets too high (higher even than the decomposition temperature), it may be lowered by introducing flexible ("spacer") groups near the rigid parts [22]. Thermotropic polymer liquid crystals often possess an even richer phase diagram than their low molecular weight counterparts because the chain connectivity causes new effects. When these polymers are applied as plastics, the liquid crystalline order can be frozen in and may give rise to new material properties like ultra-high strength [23].

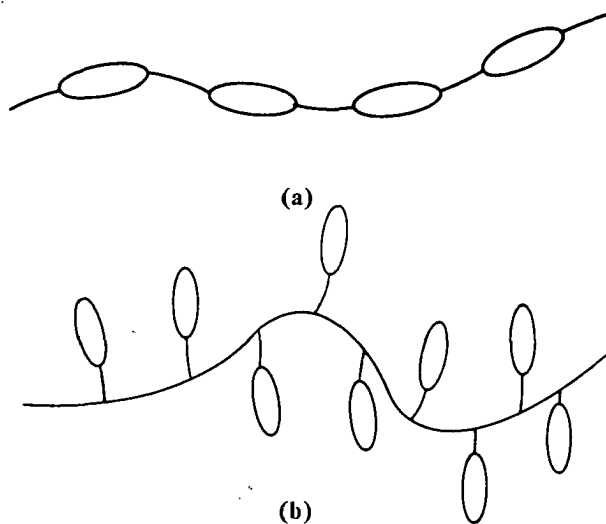


Fig. 5 (a) *Main-chain LCP* (b) *Side-chain LCP*

A different class of LCP's consists of intrinsically stiff polymers [6,7,17,24,25] (which therefore also belong to the main-chain LCP's). Apart from

the above-mentioned thermotropic behavior (like e.g. some cellulose derivatives possess) we find a new kind of phase transition in this group: in suitable solvents a liquid crystal is formed above a certain concentration of the dissolved polymer. Such a phase is called a *lyotropic* liquid crystal. The first examples of these phases were already reported as early as the twenties from inorganic colloids [26]. Polymers of this kind can be obtained from biological sources or may be purely synthetic:

- DNA [27-29]
- polysaccharides like schizophyllan [30,31] and xanthan [32]
- synthetic, helicoidal polypeptides [7,24] (e.g. poly- γ -benzylglutamate PBG)
- polyaramides [33-36] like polybenzamides

but lyotropics may even be formed from anisometric, supermolecular particles such as:

- some stiff viruses (e.g. Tobacco Mosaic Virus TMV [37-39] or fd-virus [40])
- rodlike micelles [41]
- inorganic crystallites (e.g. V_2O_5 [26] or FeOOH [26,42,43])

The number of known lyotropic liquid crystal phases is somewhat more restricted than for low molecular weight liquid crystals. However, the nematic phase and the cholesteric phase (for chiral molecules) are common, the smectic A phase is found for a number of compounds (TMV [38,39], FeOOH [42,43], [44] etc.) and even a columnar phase has been reported (TMV [45]). In micellar systems the phase diagram is often very complex, because the form of the constituent micelles itself may change with composition. In this thesis we will only deal with particles of constant intrinsic structure.

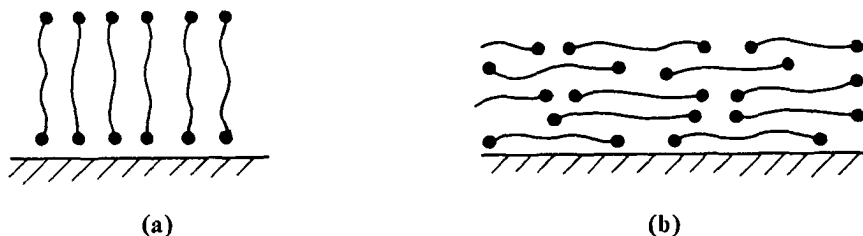


Fig. 6 A polymer liquid crystal near a wall (dots indicate the end points of the polymers) (a) perpendicular arrangement (b) parallel arrangement

Despite many similarities there are some clear distinctions between lyotropic polymer liquid crystals and low molecular weight liquid crystals. The first is the presence of solvent in lyotropics, which implies on the one hand that the particles are much further apart and on the other hand that the interaction between them will be mediated by the solvent. The second distinction is the long length of macromolecules which causes some new effects mainly concerned with entropy. As a simple example [46] consider a polymer liquid crystal near an interface and compare perpendicular and parallel

alignment of the director to the interface respectively (see fig. 6 a/b). In the perpendicular arrangement many chain ends are confined near the interface if the density is to remain constant, which is entropically unfavorable because of the very low "concentration" of chain ends in the bulk as a consequence of the large molecular length. This effect is absent for parallel alignment. Therefore, for inert interfaces (like teflon or the free surface with air) we always expect parallel alignment. The only way to obtain the perpendicular configuration is a compensating interaction energy between the wall and the chain end. However, this will occur much less often than for small molecules because there the interaction energy will be of the same order of magnitude as in the polymer case whereas the unfavorable entropy effect is absent.

Another example [46] is the splay elastic constant K_1 for liquid crystals consisting of rods. Meyer [46] pointed out that there is an entropic contribution because of the following effect: when we naively apply a splay distortion to a uniform sample (fig. 7a) the density seems to change (fig. 7b), which is compensated by other molecules filling the gap (fig. 7c). Consequently, the concentration of "bottom" ends is raised and the concentration of "top" ends lowered (fig. 7d) which is entropically unfavorable. This contribution to the splay constant even diverges for infinitely long rods: there are no chain ends to fill the gap. In low molecular weight liquid crystals this effect is negligible.

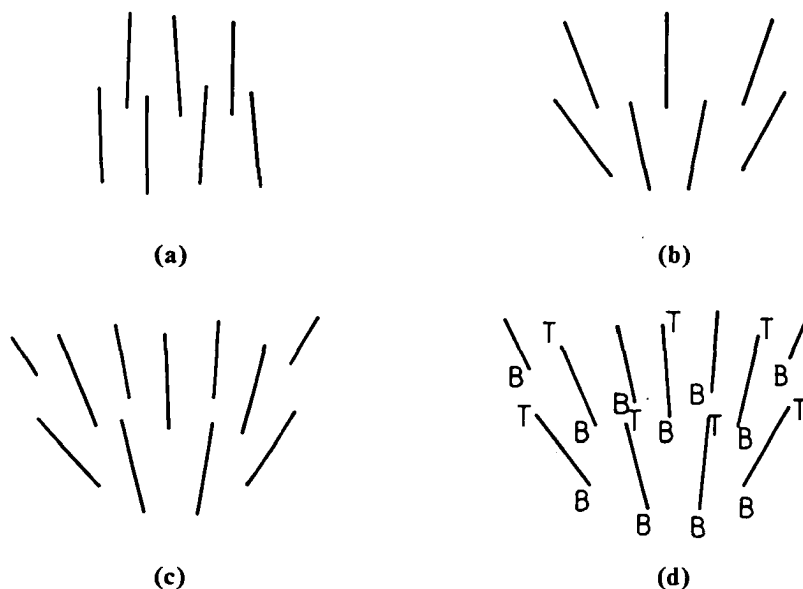


Fig. 7 Splay in a liquid crystal consisting of rodlike polymers (see text for further explanation; T: top end, B: bottom end of a polymer)

I.3 Virial Theories

The first realistic theory for the formation of nematic lyotropic liquid crystals was developed by Onsager in the early forties [47], published in his basic paper of 1949 [48]. He was inspired by the discovery of lyotropic liquid crystals for TMV [37] in a suspension of about 2% volume fraction. He modelled the particles as rigid rods and - with the low concentrations in mind - drew an analogy between the suspension and a dilute gas by formulating a virial series for the free energy (where the second virial term represents two-particle interactions, the third virial term three-particle interactions etc.). However, a collection of rods differs from a monatomic gas in the fact that the orientation of the rods is important: the virial coefficients will now depend on the orientational distribution of the rods (which is different in the isotropic and nematic states) and moreover an (orientational) entropy emerges because not all orientations are equivalent anymore. Onsager truncated the virial series after the second virial term (i.e., he only took into account two-particle interactions) and considered steric interactions between two rods. In that case the second virial coefficient B_2 is directly proportional to the excluded volume between two rods [48,1] (see fig. 8, both rods have length L and diameter D)

$$B_2 = \frac{1}{2}V_{\text{exc}} = L^2 D \sin \gamma \quad (\text{I.3.1})$$

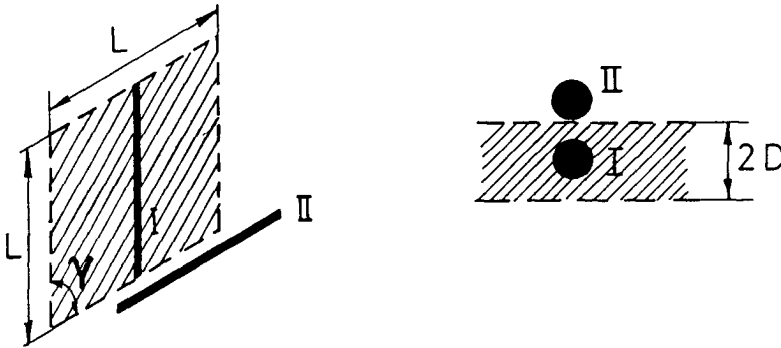


Fig. 8 Area $L^2 \sin \gamma$ (left) excluded to rod II as a result of the presence of rod I when their centerlines are within distance D from one another (right), so the excluded volume is given by $V_{\text{exc}} = 2L^2 D \sin \gamma$

As we might expect, two rods obstruct each other less for smaller mutual angles γ . Since on the other hand the orientational entropy is most favorable for an isotropic distribution, Onsager looked at the balance between orientational entropy and two-particle interactions: above a certain concentration the decrease in obstruction outweighs the loss in entropy so that a nematic is formed. The

phase transition is first order and takes place at a volume fraction ϕ of the order of

$$\phi \sim D/L \quad (I.3.2)$$

(the reason for this is the fact that the excluded volume (I.3.1) is much larger than the volume of the rods themselves which scales like LD^2). Above this volume fraction the solution segregates in an isotropic and a nematic phase. On adding more molecules the composition of each phase remains constant but the relative volume of the nematic phase increases at the expense of the isotropic phase. Above a certain concentration only the nematic phase remains. Eq. (I.3.2) implies that with increasing aspect ratio L/D , the phase transition shifts to lower and lower concentrations. This seems to justify the neglect of higher virial coefficients at least for very slender rods. Monte Carlo calculations [49] show that for L/D very large the higher virial coefficients are negligible (this has been checked up to B_5).

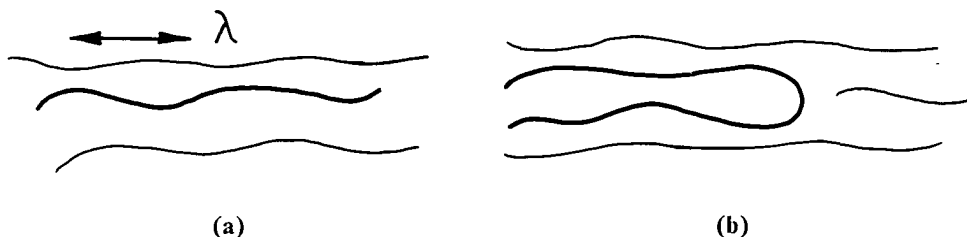


Fig. 9 (a) *Undulations of a polymer chain around the director*
(b) *A polymer chain containing a hairpin bend*

Although the Onsager model predicts an isotropic-nematic transition, it seems dubious whether LCP's can be represented by rigid rods without any flexibility. For this reason Khokhlov and Semenov [50,51] considered a wormlike chain as a model for an LCP, which can be seen as a continuous elastic cylinder with a constant elastic bending modulus (where the bending in dilute solution takes place on the scale of a persistence length P ; for a more extensive discussion of the properties of wormlike chains see the next chapter). Now the polymers are able to bend and this gives an opportunity to increase the entropy in two ways: either to undulate around the director (see fig. 9a) or even to form hairpin bends [52] (fig. 9b). Note that the undulations in fig. 9a may not be too large: because of the influence of its neighbors the chain is deflected back to the director. The length scale of these deflections is characterized by the deflection length λ [53,9], which can be shown to be much smaller than the persistence length P . The interaction between the polymers is again taken in the second virial approximation and can be shown to be the same as for rods if they are stiff and slender enough (which here implies $P \gg D$). With the new expression

for the entropy the phase transition can again be calculated to be first order and now it occurs near

$$\phi \sim D/P \quad (I.3.3)$$

for $L \gg P$. We now have an expression for two limits $L \gg P$ and $P \gg L$ (viz. for rigid rods), while both L and P must be $\gg D$. In the intermediate regime only interpolation formulas exist [51,9] (see fig. 10).

Other developments of the second virial theory include the extension to bidisperse systems [9,54,55] (mixtures of polymers with two different lengths) and polydisperse systems [9,56], determination of the elastic constants [57-59], the surface tension [60,61] and the effect of charge on the phase transition for rods [62,63]. In this thesis we discuss the elastic constants for polyelectrolytes (charged polymers) in chapter III and in chapter IV we reanalyze the case $L \gg P$ for uncharged, semiflexible polymers by solving the problem exactly, obtaining the coefficients in (I.3.3) for the isotropic and anisotropic transition concentrations. In addition, we study the occurrence of hairpins [52,64] in the nematic state and their effect on the splay elastic constant. In chapter V these results are extended to polyelectrolytes.

At the end of this section it may be worthwhile to mention the restrictions and advantages of the virial theories:

- The second virial approximation only works for low volume fraction, which is coupled to the asymmetry ratios L/D and P/D by formulas (I.3.2) and (I.3.3) or their extensions. Quantitatively, this is only justified for very large values of these ratios (on the order of 100). Qualitatively, we may expect that the theory will not work for ratios smaller than 20 (implying volume fractions of about 0.25 at the isotropic-nematic transition).
- The original versions only considered steric interactions and thus do not give a temperature dependence. Although extensions to charged systems have been given, the influence of Van der Waals forces has not been considered in detail yet.
- The influence of flexibility has been described by the wormlike chain model. Although this model will probably not work for all polymers, we know it works for the usual stiff polymers. Besides, it is possible to test this supposition for any specific polymer by several independent measurements in dilute solution.
- The nematic order is not allowed to be too high (then eq. (I.3.1) would have to be modified and higher virial coefficients be included).
- Finally, the greatest advantage of the virial theories is the fact that they are based on a very clear physical picture and all approximations used are well-understood and can be made small in an experiment. Consequently, the theory does *not* have any adjustable parameters, which allows for a stringent test.

I.4 Experimental Support for the Virial Theories

In his review article Odijk [9] also discussed some of the few trustworthy experiments to test the above theories. These include extensive measurements on the polysaccharide schizophyllan [30,31] (solvent H_2O , $P \approx 2000 \text{ \AA}$, $D \approx 16.7 \text{ \AA}$) and on the polypeptide poly- γ -benzyl-L-glutamate [7] (PBLG, solvent dioxane + 4% trifluoroacetic acid, $P \approx 800 \text{ \AA}$, $D \approx 15.5 \text{ \AA}$). Both molecules are chiral and give a cholesteric phase instead of a nematic. Since the chiral interactions are extremely small and the pitch is large we assume that we can apply the theory for nematics. For both compounds the transition concentrations can be predicted to within 20% provided semiflexibility is taken into account (note that this is essential even for the samples with $L < P$). For schizophyllan experiments on bidisperse samples [30,31] can also be explained satisfactorily. However, experiments on the very stiff TMV [37-39] can not be explained because of a too low axial ratio $L/\tilde{D} \approx 10$, which requires inclusion of higher virial coefficients (the effective diameter $\tilde{D}$ is somewhat larger than the actual diameter because of the charge present on TMV). The same is true for semiflexible DNA in 0.1 M NaCl/ H_2O [29] because of a too low ratio $P/\tilde{D} \approx 12$.

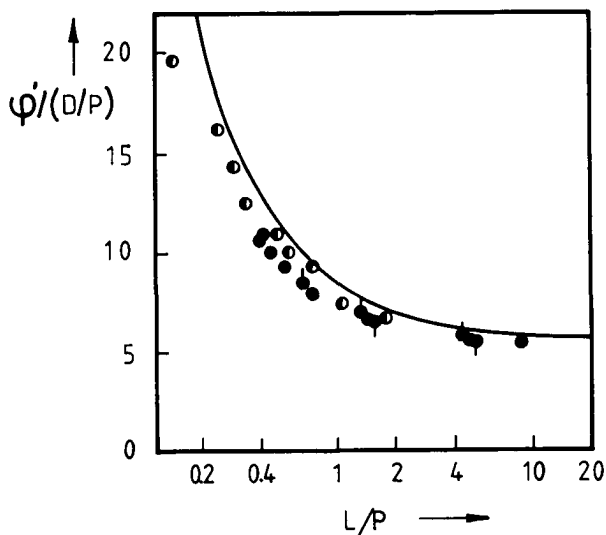


Fig. 10 Comparison [65] of measured and theoretical values for ϕ' (volume fraction at which a liquid crystalline phase begins to appear) as a function of chain length for polyhexylisocyanate in toluene ● (10°C), ◐ (25°C), ▼ (40°C) and for schizophyllan in water ○ (25°C). The solid line gives the theoretical interpolation formula [51] as modified in ref. 9.

Since then some new experiments have been performed, which we will review now. To further test the semiflexibility theory Ito and Teramoto [65] chose to study a less rigid polymer than schizophyllan and PBLG, viz. polyhexylisocyanate (PHIC). In toluene this polymer has a persistence length ranging from $410 \text{ \AA}$ (10°C) to $340 \text{ \AA}$ (40°C) and in dichloromethane $P \approx 210 \text{ \AA}$ (20°C), while its diameter is $12.5 \text{ \AA}$. They prepared 7 nearly monodisperse samples in the range $L = 150\text{--}3300 \text{ \AA}$ and determined the phase transition concentrations by measuring the volumes of the isotropic and anisotropic phase for different concentrations situated in the biphasic gap. The results in toluene are consistently somewhat lower than the interpolation formulas and the corresponding points for schizophyllan (see fig. 10) but the difference remains less than 10%. For the polymer in dichloromethane the agreement gets worse, which may be attributed to the increasing influence of higher virial coefficients (note that $P/D \approx 17$ which is rather low). So we might conclude that these measurements fit excellently in the framework of the semiflexible virial theories, whereas the rodlike theory fails completely. Other measurements [66] on the same polymer in the same solvents seem to be in disagreement with the above results and the virial theory. However, samples used in that study were polydisperse which may influence the results considerably and transition concentrations were mainly determined visually by noting the appearance of birefringence under a polarizing microscope. This illustrates the need for very careful experiments to assess the theories.

Other developments have taken place on PBLG. In a review article DuPré and Parthasarathy [67] summarize experimental results for the phase transition in various solvents (inducing different persistence lengths in PBLG) and compare them with lattice theories [68] and semiflexible virial theories [51,9]. They conclude that both theories predict values which are too low compared with the experimental results (depending on the solvent up to 50% for the virial theories and up to 70% for the lattice theory). Lattice theory seems to do somewhat better if $L < P$ while the virial theory performs markedly better if $L > P$.

The Brandeis group [69,70] measured the elastic constants and the anisotropic viscosities of PBG in 18% dioxane/ 82% dichloromethane (a solvent mixture which greatly reduces the cholesteric twist, a small amount of DMF was added to prevent aggregation of the polymers) as a function of concentration and chain length. The technique they applied was quasielastic depolarized Rayleigh scattering. We summarize existing theories for the elastic constants (within the second virial approach) and experimental results in Table 1.

The length dependence was determined in the regime $L \approx 0.5\text{--}1.5 P$ (for about 9 different lengths) and the concentration dependence only at the lowest value of L for 6 different volume fractions between 15 and 32%. The length dependence of K_1 is linear in accordance with theory which predicts the same dependence in both the rodlike and semiflexible regimes. The value of K_2 is

assumed to change very little and is used as an input in obtaining the other two constants. K_3 seems to change near $L \simeq P$ from a strong dependence on L to a much weaker dependence. Lee [70] then concludes that the behavior changes from rodlike to semiflexible. However, this does not agree with the dependence on volume fraction for the shortest molecule [69], which already seems to behave like a semiflexible chain. Note that the contour length is much larger than the deflection length λ , which also implies some influence of flexibility (see next chapter). The absolute magnitude of K_1 and K_3 is of the same order (10^{-6} dynes) while K_2 is much smaller (10^{-8} - 10^{-7} dynes). It is difficult to draw definitive conclusions from the results for the anisotropic viscosities, because the theory is not well developed yet, though it is clear that rodlike models do not work [69,70].

	THEORY [46,58]		EXPERIMENT [69,70]	
	rod	semiflexible	$\phi \simeq 0.16$	$L \simeq 0.5P$
K_1	$\phi[L/D]$	$\phi[L/D]$	L^1	ϕ^1
K_2	$\phi[L/D] (<\frac{1}{3}K_1)$	$\phi^{1/3}[P/D]^{1/3}$	L^0	$\phi^0 (<< K_1, K_3)$
K_3	$\phi^3[L/D]^3$	$\phi[P/D]$	$L \lesssim P$: strong $L \gtrsim P$: weak	ϕ^1

Table 1 Comparison of theoretical and experimental results for the elastic constants of PBLG

Recently, Parthasarathy et al. [71] also determined the length dependence of the elastic constants of PBLG in various other solvents (dioxane, cyclohexanone, m-cresol and nitrobenzene) by measuring the cholesteric-nematic transition and the Frederiks transition in a magnetic field. They find results totally different from those of the Brandeis group, although they use very similar molecular weights and comparable volume fractions. The length dependence is somewhat blurred by the fact that they did not use equal volume fractions for all molecular weights but chose a concentration just above the phase transition (which is itself length dependent). Furthermore, in most solvents they only obtained the values for three different molecular weights. Nevertheless we can make some observations:

- the ratio K_1/K_3 is of the order of 100 while in most solvents $K_1 \gg K_2 > K_3$ (except in cyclohexanone where $K_1 > K_3 > K_2$)
- the length dependence of K_1 is not clear, for some solvents it increases for others it decreases as a function of molecular weight

- K_2 is certainly not constant but generally increases with length
- K_3 does not change in any systematic way
- for the various solvents the results can differ by a factor of 5
- there is much scatter in the results

The authors ascribe some of the differences to a change in conformation of the side groups. In the literature [46,72] the determination of elastic constants of lyotropic polymer liquid crystals by the Frederiks transition is disputed because of the occurrence of complicated nonlinear effects. So, unfortunately, these experiments do not shed much light upon the theories, except that a rodlike model would be worst. Apparently, a lot of careful, systematic research should be done.

As becomes clear from the above discussion, we are beginning to understand some of the experiments. Apart from the scientific interest in itself, this is also relevant from a technological point of view. An important application is for instance the spinning of fibers. Eventually, one would like to be able to describe flow phenomena like those occurring in the spinning process [23]. Here, a liquid crystalline solution is forced through a very small hole after which it is coagulated as a ultra-high strength fiber (like e.g. the polyaramide fibers Kevlar and Twaron). Since the strength critically depends on the degree of orientation - which is influenced both by the equilibrium properties and by the flow - the determination and understanding of phase transitions, elastic constants and viscosities is important.

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CHAPTER II

THEORETICAL BACKGROUND

In this chapter we will elucidate or derive some of the expressions which we will use as starting equations in later chapters.

II.1 Virial Expansion of the Free Energy of Rodlike Particles

To show the analogy between a lyotropic liquid crystal and a dilute gas we start with the virial expansion [1] of the Helmholtz free energy ΔF for a gas of N_L particles and (number) density ρ_L at absolute temperature T

$$\frac{\Delta F}{N_L k_B T} = \ln \rho_L - 1 + B_2 \rho_L + \frac{1}{2} B_3 \rho_L^2 + \dots \quad (\text{II.1.1})$$

where k_B is Boltzmann's constant. $\ln \rho_L - 1$ is the ideal gas term, subsequent terms represent two-, three- and more-particle interactions. According to Mayer cluster expansion theory [1], the virial coefficients B_n can be expressed as irreducible cluster integrals β_{n-1} of the Mayer-functions

$$\Phi_{12} \equiv \exp(-u_{12}/k_B T) - 1 \quad (\text{II.1.2})$$

defined in terms of the two-body potential u_{12} (three-body potentials are neglected throughout). The first two virial coefficients can be written as follows

$$B_2 = -\frac{1}{2} \beta_1 \equiv -\frac{1}{2V} \iint \Phi_{12} dr_1 dr_2 = -\frac{1}{2} \int \Phi_{12} dr_{12} \quad (\text{II.1.3})$$

$$B_3 = -\frac{2}{3} \beta_2 \equiv -\frac{1}{3V} \iiint \Phi_{12} \Phi_{23} \Phi_{31} dr_1 dr_2 dr_3 \quad (\text{II.1.4})$$

For a mixture of s different gases with mole fractions x_i such that

$$\sum_{i=1}^s x_i = 1 \quad (\text{II.1.5})$$

it is easy to extend eq. (II.1.1), keeping the total number of particles N_L and the number density ρ_L constant

$$\frac{\Delta F}{N_L k_B T} = \ln \rho_L - 1 + \sum_{i=1}^s x_i \ln x_i + B_2 \rho_L + \frac{1}{2} B_3 \rho_L^2 + \dots \quad (\text{II.1.6})$$

where $\sum x_i \ln x_i$ stems from the entropy of mixing [1]. However, the virial coefficients are now slightly more complicated, e.g. [2,3]

$$B_2 = -\frac{1}{2} \sum_{i,j=1}^s x_i x_j \beta_1(i,j) \quad (\text{II.1.7})$$

because there are different cluster integrals for the various possible combinations of particles

$$\beta_1(i,j) \equiv \frac{1}{V} \iint \Phi_{12}(i,j) dr_1 dr_2 = \int \Phi_{12}(i,j) dr_{12} \quad (\text{II.1.8})$$

where the Mayer function $\Phi_{12}(i,j)$ is an extension of eq. (II.1.2) by replacing u_{12} by the two-body potential for particles of type i and j , $u_{12}(i,j)$.

Onsager [3] argued that a solution of elongated particles in a solvent is similar to a gas when we replace the two-body potential u_{12} between two gas molecules by the potential of mean force w_{12} between two particles [4] (which means that an average over all solvent configurations has taken place). This implies, however, that this potential of mean force depends on the chemical potential μ_o of the solvent, which should preferably be kept constant only adding a constant term $\mu^o(T, \mu_o)$ to the free energy. In principle, experiments are therefore best done in dialytic equilibrium with pure solvent, which has practical implications in the case of mixed solvents. For suspensions of spherical particles it is possible to use eq. (II.1.1) as a basic equation but for anisometric particles not all directions are equivalent and the potential of mean force $w_{12}(r_{12}; \Omega, \Omega')$ will now also depend on their orientations (determined by the solid angles Ω and Ω'). Onsager [3] considered particles of different directions as being of different type and defined an angular distribution function $f(\Omega)$ which is a continuous analogue of the mole fractions x_i . Eqs. (II.1.5-8) can then be replaced by [34]

$$\int f(\Omega) d\Omega = 1 \quad (\text{II.1.9})$$

$$\frac{\Delta F}{N_L k_B T} = \frac{\mu^o(T, \mu_o)}{k_B T} + \ln \rho_L - 1 + \int f(\Omega) \ln[4\pi f(\Omega)] d\Omega + B_2 \rho_L + \frac{1}{2} B_3 \rho_L^2 + \dots \quad (\text{II.1.10})$$

$$B_2 = -\frac{1}{2} \iint f(\Omega) f(\Omega') \beta_1(\Omega, \Omega') d\Omega d\Omega' \quad (\text{II.1.11})$$

$$\beta_1(\Omega, \Omega') \equiv \frac{1}{V} \iint \Phi_{12}(r_{12}; \Omega, \Omega') dr_1 dr_2 = \int \Phi_{12}(r_{12}; \Omega, \Omega') dr_{12} \quad (\text{II.1.12})$$

$\Phi_{12}(r_{12}; \Omega, \Omega')$ is again an extension of eq. (II.1.2) by replacing u_{12} with $w_{12}(r_{12}; \Omega, \Omega')$. The factor 4π in the entropy of mixing is introduced for convenience to make this term zero for an isotropic distribution $f(\Omega) = 1/4\pi$. Although we write $f(\Omega)$ in the above, in a nematic the distribution function will only depend on θ the angle with the director and not on the azimuthal angle ϕ , because of the symmetry of the nematic phase. Onsager [3] proceeded by truncating the virial expansion after the second virial term, which is only valid for low densities ρ_L . The influence of the third virial coefficient was discussed by Straley [5] and Odijk [6].

In order to evaluate the second virial coefficient we have to know the cluster integral $\beta_1(\Omega, \Omega')$. This is obtained very easily for a hard-core interaction using eq. (II.1.2)

$$\begin{aligned} w_{12} &= \infty & \Phi_{12} &= -1 & \text{for overlapping configurations} \\ w_{12} &= 0 & \Phi_{12} &= 0 & \text{for non-overlapping configurations} \end{aligned} \quad (\text{II.1.13})$$

When we substitute these values for Φ_{12} in eq. (II.1.12) we find that for hard-core interactions β_1 is just the negative of the excluded volume. For two rods of length L and diameter D at an angle of γ this was determined in fig. 8 of chapter I [3,7]

$$\beta_1(\Omega, \Omega') = -2L^2 D \sin \gamma \quad (\text{II.1.14})$$

For an isotropic distribution this gives for B_2 the value $\frac{\pi}{4} L^2 D$. It is convenient to scale the density with this volume obtaining the dimensionless concentration

$$c_L \equiv \frac{\pi}{4} L^2 D \rho_L \quad (\text{II.1.15})$$

Further defining

$$\sigma(f) \equiv \int f(\Omega) \ln[4\pi f(\Omega)] d\Omega \quad (\text{II.1.16})$$

$$\rho(f) \equiv \frac{4}{\pi} \int \int f(\Omega) f(\Omega') \sin \gamma d\Omega d\Omega' \quad (\text{II.1.17})$$

we now have a short-hand notation for the free energy

$$\frac{\Delta F}{N_L k_B T} = \text{cst} + \ln c_L + \sigma(f) + c_L \rho(f) \quad (\text{II.1.18})$$

II.2 Phase Transition for Rodlike Particles

To obtain the distribution function $f(\Omega)$ there are two lines we can follow. The simplest is to choose a trial function with one or more variational parameters, calculate the free energy and minimize the resulting expression with respect to the variational parameters. Onsager [3] made a very clever one-parameter guess

$$f(\alpha) = \frac{\alpha}{4\pi} \frac{\cosh(\alpha \cos \theta)}{\sinh(\alpha)} \quad (\text{II.2.1})$$

with which asymptotic expansions - valid for large α - for σ and ρ can be obtained. A simpler version, giving the same leading order terms for these expansions, is the so called Gaussian distribution function [6]

$$\begin{aligned} f(\alpha) &= \frac{\alpha}{4\pi} \exp(-\frac{1}{2}\alpha\theta^2) & (0 \leq \theta < \pi/2) \\ \text{and} &= \frac{\alpha}{4\pi} \exp(-\frac{1}{2}\alpha(\pi-\theta)^2) & (\pi/2 < \theta \leq \pi) \end{aligned} \quad (\text{II.2.2})$$

Both trial functions (II.2.1) and (II.2.2) give the following exact leading order relation between α and c_L upon minimizing eq. (II.1.18)

$$\alpha \sim \frac{4c_L^2}{\pi} \quad (\text{II.2.3})$$

The more exact way to acquire $f(\Omega)$ is to minimize expression (II.1.18) for arbitrary variations in f under the condition that the normalization (II.1.9) is fulfilled. This yields a nonlinear integral equation [3]

$$\ln[4\pi f(\Omega)] = E - \frac{8}{\pi} c_L \int \sin \gamma f(\Omega') d\Omega' \quad (\text{II.2.4})$$

where E is a Lagrange multiplier which can be determined by applying eq. (II.1.9) to the solution. Various methods have been devised to solve eq. (II.2.4) either with the help of Legendre expansions and numerical integration [8-10] or by purely numerical integration [11]. Apart from the isotropic solution $f(\Omega) = 1/4\pi$, also anisotropic solutions are found above a certain value of c_L .

To determine the phase transition from an isotropic to an anisotropic state we need to know the osmotic pressure Π and the chemical potential μ

$$\Pi = -\left. \frac{\partial \Delta F}{\partial V} \right|_{N_L, \mu_o, T} = k_B T \rho_L [1 + c_L \rho(f)] (= k_B T [\rho_L + B_2 \rho_L^2]) \quad (\text{II.2.5})$$

$$\mu = \left. \frac{\partial \Delta F}{\partial N_L} \right|_{V, \mu_o, T} = \mu^o + k_B T [\ln \rho_L + \sigma(f) + 2c_L \rho(f)] \quad (\text{II.2.6})$$

which must be equal in both phases (isotropic and anisotropic phase, indicated by subscripts i and a respectively), giving the coexistence equations

$$c_{L,i} (1 + c_{L,i}) = c_{L,a} (1 + c_{L,a} \rho_a) \quad (\text{II.2.7})$$

$$\ln c_{L,i} + 2c_{L,i} = \ln c_{L,a} + \sigma_a + 2c_{L,a} \rho_a \quad (\text{II.2.8})$$

Eqs. (II.2.4), (II.2.7) and (II.2.8) can then be solved iteratively to give [8-11] $c_{L,i} = 3.290$, $c_{L,a} = 4.191$, $\sigma_a = 1.602$, $\rho_a = 0.5651$ and order parameter $S = 0.7922$.

II.3 Elastic Constants for Rodlike Particles

In the preceding section we described the direction of the rodlike molecules with a single distribution function, implicitly assuming that the director is uniform over the whole sample. From eq. (I.1.2) we see that this is no longer the case if we want to determine the elastic moduli. Following Priest [12] we can divide the effect of non-uniformity in two parts:

- the distribution function at each point must be determined with respect to the local director
- the form of the distribution function may change.

The last effect may be neglected, which can be seen by considering a small periodic distortion of the director characterized by a small wave vector $\mathbf{q}$. From eq. (I.1.2) we see that the elastic moduli are the coefficients of the q^2 term in the free energy. In fig. 1 we show that the transformation $\mathbf{q} \rightarrow -\mathbf{q}$ has the same effect on the director pattern as the transformation $\mathbf{n} \rightarrow -\mathbf{n}$. Thus - as a result of the equivalence of $\mathbf{n}$ and $-\mathbf{n}$ in a nematic - the correction to the distribution function must be of order q^2 . However, the free energy is an absolute minimum for arbitrary changes in the distribution function, whence the correction to the free energy will be of order q^4 and give no contribution to the elastic constants.

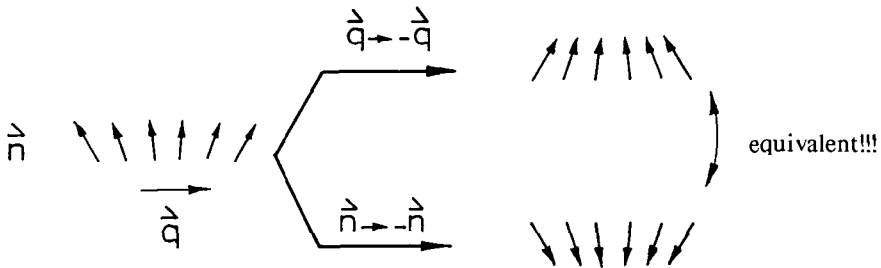


Fig. 1 Illustration of the equivalence of $\mathbf{q} \rightarrow -\mathbf{q}$ and $\mathbf{n} \rightarrow -\mathbf{n}$ for the case of splay deformation

This means that we can retain the equilibrium distribution function on the understanding that it is peaked around the local director everywhere. Because this merely rotates the distribution there will be no consequence for the orientational entropy but only for the two-particle interaction term, which is generalized from eqs. (II.1.10-12) to give the excess free energy ΔF_d for a slightly distorted director pattern with respect to a uniform director field

$$\frac{\Delta F_d}{N_L k_B T} = -\frac{1}{2V\rho_L} \iiint \Phi_{12}(\mathbf{r}_{12}; \Omega, \Omega') [f(\cos\theta'(\mathbf{r}_1 + \mathbf{r}_{12})) - f(\cos\theta'(\mathbf{r}_1))] \times \\ f(\cos\theta(\mathbf{r}_1)) d\Omega d\Omega' d\mathbf{r}_{12} \quad (\text{II.3.1})$$

Straley [13] proposed a Taylor expansion of $f(\cos\theta'(\mathbf{r}_1 + \mathbf{r}_{12}))$ to second order in $\mathbf{r}_{12}$ and managed to perform the integral over $\mathbf{r}_{12}$ using eq. (II.1.13) and under the condition $D \ll L$ - the same restriction under which the second virial theory applies. By partial integration Straley [13] then brought eq. (II.3.1) in a form similar to eq. (I.1.2) and was able to identify the elastic moduli. Here, we give the further simplified form due to Odijk [14]

$$K_i = -\frac{k_B T}{D} \frac{4c_L^2}{3\pi^2} \iint f'(\cos\theta) f'(\cos\theta') \sin\gamma H_{i,0} d\Omega d\Omega' \quad (\text{II.3.2})$$

where the factor $H_{i,0}$ depends on the directions of the two rods in a fashion typical of the deformation at hand

$$H_{1,0} = 3H_{2,0} = \frac{3}{4} \sin^2\theta \sin\theta' \cos(\phi - \phi') \quad (\text{II.3.3a})$$

$$H_{3,0} = \cos^2\theta \sin\theta \sin\theta' \cos(\phi - \phi') \quad (\text{II.3.3b})$$

Using Gaussian distribution function (II.2.2), Odijk [14] determined the leading order behavior of the elastic constants

$$K_1 (= 3K_2) \sim \frac{k_B T}{D} \frac{7c_L}{8\pi} \quad (\text{II.3.4a})$$

$$K_3 \sim \frac{k_B T}{D} \frac{4c_L^3}{3\pi^2} \quad (\text{II.3.4b})$$

Apart from the two-particle part (cf. eq. (II.3.1)) described above, the splay elastic constant also contains a one-particle contribution [15] as sketched in section I.2. Starting from a uniform nematic a uniform splay can be obtained by rotating the rods by different angles about their centers (which keeps the density ρ_L of the centers constant as well as the form of the distribution function). It can be shown that in this procedure the volume available to the bottom ends of the rods is decreased by a factor $[1 - \frac{1}{2}L\nabla \cdot \mathbf{n}]$ giving a density of bottom ends ρ_b of

$$\rho_b \simeq \frac{\rho_L}{1 - \frac{1}{2}L\nabla \cdot \mathbf{n}} \quad (\text{II.3.5})$$

This inhomogeneity in the density leads to an extra term in the free energy

$$\frac{\Delta F}{V} \simeq \frac{1}{2} k_B T \frac{(\rho_b - \rho_L)^2}{\rho_L} \stackrel{(II.3.5)}{\simeq} \frac{1}{2} k_B T \frac{L^2 \rho_L}{4} (\nabla \cdot \mathbf{n})^2 \quad (II.3.6)$$

Comparing with eq. (I.1.2) we see that this gives an extra contribution to the splay constant:

$$\Delta K_1 \simeq \frac{1}{4} L^2 \rho_L k_B T \stackrel{(II.1.15)}{=} \frac{k_B T}{D} \frac{c}{\pi} \quad (II.3.7)$$

which is about as large as the two-particle term (II.3.4a).

II.4 Wormlike Chains

In the above sections we only considered rodlike molecules, whereas in reality even stiff polymers will have some degree of flexibility. A well-established model for polymers is the wormlike chain [16,17] which interpolates between the random-flight chain and the rod. With this model many different experiments in dilute solution have been explained [18]. The wormlike chain can be seen as the continuous version of the freely rotating chain - consisting of N links of length a with a fixed bond angle ψ between adjacent links - taken in the following limit [17]

$$\lim_{\substack{N \rightarrow \infty \\ a \rightarrow 0}} Na = L \quad (II.4.1)$$

$$\lim_{\substack{\psi \rightarrow \pi \\ a \rightarrow 0}} \frac{a}{1 + \cos \psi} = P \quad (II.4.2)$$

P is called the (intrinsic) persistence length because it is the typical length over which the correlation between the tangential vectors $\mathbf{v}$ at two points s and t "persists" (see fig. 2) [17]:

$$\langle \mathbf{v}(s) \cdot \mathbf{v}(t) \rangle = \langle \cos \theta(t-s) \rangle = \exp(-|t-s|/P) \quad (II.4.3)$$

where distances s and t are measured from one end of the chain along its contour and the pointed brackets denote an ensemble average. As a measure of the stiffness of the chain the persistence length is also directly related to the elastic bending constant [17]

$$\epsilon = P k_B T \quad (II.4.4)$$

Because the local radius of curvature R_c is coupled to the change in direction $R_c = \dot{\mathbf{v}}(s)^{-1} = [\partial \mathbf{v} / \partial s]^{-1}$ the energy of bending is given by [17]

$$\Delta F_b = \frac{1}{2} \int_0^L \frac{\epsilon}{R_c^2} ds = \frac{1}{2} P k_B T \int_0^L \dot{v}^2(s) ds \quad (\text{II.4.5})$$

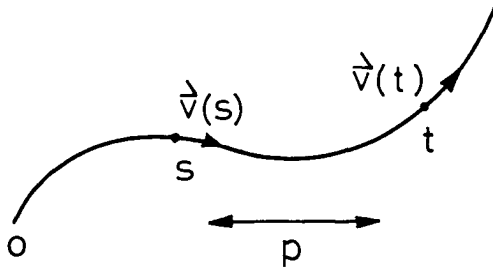


Fig. 2 wormlike chain with an indication of the persistence length P (see text)

Let us now consider a wormlike chain in an external potential $U_{\text{ex}}(v)$ (per unit chain length). We may then write the partition function with the chain ends fixed as a path integral over all configurations [6,17,19]

$$Z(v_1, v_2, L) = \int_{v(0)=v_1}^{v(L)=v_2} \exp \left[-\frac{1}{2} P \int_0^L \dot{v}^2(s) ds - \int_0^L \frac{U_{\text{ex}}(v(s))}{k_B T} ds \right] \mathcal{D}[v(s)] \quad (\text{II.4.6})$$

The total partition function Z_{tot} can be obtained by integration over v_1 and v_2 . Analogously to the path integral formalism in quantum mechanics eq. (II.4.6) formally corresponds to a Schrödinger type equation [6,17,19-21]

$$\frac{\partial Z(v_1, v, s)}{\partial s} = \frac{1}{2P} \Delta_v Z(v_1, v, s) - \frac{U_{\text{ex}}(v)}{k_B T} Z(v_1, v, s) \quad (\text{II.4.7})$$

with boundary condition $\lim_{s \rightarrow 0} Z(v_1, v, s) = \delta(v - v_1)$, which implies that $Z(v_1, v, s)$ is a Green function. Δ_v is the angle dependent part of the Laplacian. Alternatively eq. (II.4.7) can be seen as a diffusion equation with contour distance s playing the role of time: starting with direction v_1 the orientation of all subsequent points is determined by a diffusive process taking place on a unit sphere with a diffusion constant $(2P)^{-1}$ under influence of an external orientational potential.

$Z(v_1, v, s)$ can also be interpreted as an (unnormalized) conditional

probability function: it gives the probability of finding an orientation v at a contour distance s from the starting orientation v_1 . This may be used to derive an orientational distribution function at the point s of the chain [6,21]

$$f(v,s) = \frac{\int dv_1 \int dv_2 Z(v_1, v, s) Z(v, v_2, L-s)}{\int dv_1 \int dv_2 Z(v_1, v_2, L)} \quad (II.4.8)$$

When $L \gg P$ most of the points on the chain are far from the ends and it makes sense to use an average distribution function [6,22]

$$f(v) \equiv \frac{1}{L} \int_0^L ds f(v,s) = \frac{\int dv_1 \int dv_2 \int_0^L ds Z(v_1, v, s) Z(v, v_2, L-s)}{L \int dv_1 \int dv_2 Z(v_1, v_2, L)} \quad (II.4.9)$$

II.5 The Nematic Phase for Wormlike Chains

With eq. (II.4.7) an expression for the entropy of a wormlike chain can be derived as was first demonstrated by Khokhlov and Semenov [22] on the basis of the Lifshitz theory of polymers [23,24]. Here we will only give the derivation for very long chains ($L \gg P$) using arguments advanced by Odijk [6]. For very long chains both end points are no longer correlated so their contribution to Z factorizes. Moreover, the free energy must be extensive for long chains giving an asymptotic form [6]

$$Z(v_1, v, L) \sim e^{-\mu_0 L} \psi(v_1) \psi(v) \quad (II.5.1)$$

which is the same form one would obtain as the first term in an eigenfunction expansion. Inserted in eq. (II.4.7) this yields [6]

$$\frac{1}{2P} \Delta \psi(v) - \frac{U_{ex}(v)}{k_B T} \psi(v) + \mu_0 \psi(v) = 0 \quad (II.5.2)$$

on the other hand from eqs. (II.4.9) and (II.5.1) we can write for the distribution function

$$f(v) = \psi^2(v) \quad (II.5.3)$$

The crux of the derivation is the fact that it is possible to determine the configurational entropy ΔS_{con} from the internal energy U and the free energy, irrespective of the form of U_{ex} and the eigenvalue μ_0 . Neglecting end effects we have [6]

$$\Delta S_{\text{con}} = \frac{U - F}{k_B T} = L \frac{\langle U_{\text{ex}} \rangle}{k_B T} + \ln Z_{\text{tot}} \\ \simeq L \int f(v) \frac{U_{\text{ex}}(v)}{k_B T} dv - \mu_o L = L \int f(v) \left[\frac{U_{\text{ex}}(v)}{k_B T} - \mu_o \right] dv \quad (\text{II.5.4})$$

from which both U_{ex} and μ_o may be eliminated with the help of eq. (II.5.2)

$$\Delta S_{\text{con}} = \frac{L}{2P} \int f(v) \frac{\Delta_v \psi(v)}{\psi(v)} dv \stackrel{(\text{II.5.3})}{=} \frac{L}{2P} \int \psi(v) \Delta_v \psi(v) dv \quad (\text{II.5.5})$$

Applying the same basic ideas, Khokhlov and Semenov [21] also derived a more general expression for the entropy of wormlike chains with arbitrary L/P ratio.

In the preceding we saw that the configurational entropy for a wormlike chain is very different from the orientational entropy for rods $-\sigma(f)$ given by eq. (II.1.16). We introduce a similar short-hand notation for the configurational entropy measured per persistence length

$$\sigma_P(f) \equiv -(P/L) \Delta S_{\text{con}} = -\frac{1}{2} \int f^{1/2}(\Omega) \Delta f^{1/2}(\Omega) d\Omega = -\frac{1}{2} \int \psi(\Omega) \Delta \psi(\Omega) d\Omega \quad (\text{II.5.6})$$

where solid angle Ω is equivalent to tangential vector v and operator Δ is the same as Δ_v . On the other hand, in chapter V.2 it is argued that for stiff chains ($P \gg D$) the two-particle interaction (or second virial) term will be nearly the same as for rods. For hard-core interactions the free energy per chain may then be formulated as

$$\frac{\Delta F}{N_L k_B T} = \frac{\mu^o(T, \mu_o)}{k_B T} + \ln \rho_L - 1 + \frac{L}{P} \sigma_P(f) + \frac{\pi}{4} L^2 D \rho_L \rho(f) \quad (\text{II.5.7})$$

or alternatively as a free energy per persistence length

$$\frac{\Delta F}{N_P k_B T} = \text{cst} + \frac{P}{L} \ln c_P + \sigma_P(f) + c_P \rho(f) \quad (\text{II.5.8})$$

where $N_P \equiv (L/P) N_L$ and for semiflexible chains we have a scaled concentration

$$c_P \equiv \frac{\pi}{4} P L D \rho_L \quad (\text{II.5.9})$$

instead of c_L defined in eq. (II.1.15).

Eq. (II.5.8) forms the basis of the description of a liquid crystal consisting of long semiflexible polymers ($L \gg P \gg D$) in which limit the translational entropy $(P/L) \ln c_P$ is negligible

$$\frac{\Delta F}{N_P k_B T} \simeq \text{cst} + \sigma_P(f) + c_P \rho(f) \quad (\text{II.5.10})$$

Eq. (II.5.10) again may be solved approximately by employing trial functions such as eqs. (II.2.1) and (II.2.2), giving the exact leading order relation [6]

$$\alpha \sim \frac{4c_P^{2/3}}{\pi^{1/3}} \quad (\text{II.5.11})$$

In chapter IV, however, we will minimize eq. (II.5.10) and solve the resulting integrodifferential equation. For the phase transition [22,6], the coexistence equations corresponding to eq. (II.5.10) are determined similarly to eqs. (II.2.5-8)

$$(c_{P,i})^2 = (c_{P,a})^2 \rho_a \quad (\text{II.5.12})$$

$$2c_{P,i} = \sigma_a + 2c_{P,a} \rho_a \quad (\text{II.5.13})$$

II.6 A Scaling Approach for Nematic Wormlike Polymers

We now discuss a scaling approach of semiflexible chains due to Odijk [6,25,26]. As mentioned in the introduction (see also fig. 9a of chapter I), such a chain will show undulations around the director. At first sight one would expect that the length scale characterizing these undulations is the length associated with chain stiffness, viz. the persistence length P . Odijk argued, however, that because of the confinement of the chain in the nematic this can no longer be the case. Locally, the correlation given by eq. (II.4.3) still applies and - for the small angles and distances involved - can be represented as

$$\langle \theta^2(t-s) \rangle \sim \frac{2|t-s|}{P} \quad (\text{II.6.1})$$

But over larger distances the chain will have to comply with the fact that its angle with the director, θ , is limited because of the nematic order. For example with the Gaussian distribution function (II.2.2) the mean square of angle θ is

$$\langle \theta^2 \rangle \sim 2/\alpha \quad (\text{II.6.2})$$

So the length scale on which the chain is "deflected" back to the director, the so-called deflection length λ , is obtained by comparing (II.6.1) and (II.6.2) [6]

$$\lambda \equiv P/\alpha \quad (\text{II.6.3})$$

which is smaller than P because $\alpha \gg 1$ in the nematic state.

In a statistical sense the nematic solution of N_L long semiflexible chains can now be considered as composed of $(L/\lambda) N_L$ effective quasi-rodlike units. This leads to a scaling recipe [26]

$$L \rightarrow \lambda = P/\alpha \quad \text{and} \quad c_L \rightarrow c_\lambda = c_P/\alpha \quad (\text{II.6.4})$$

to transcribe results for rods to expressions for semiflexible chains. For example, applying this recipe to eq. (II.2.3) yields the corresponding relation (II.5.11) for semiflexible chains, apart from the multiplicative constant. Similarly, from eqs. (II.3.4) Odijk derived scaling expressions for the elastic constants of semiflexible chains [14,26]

$$K_2 \propto \frac{k_B T}{D} c_P^{1/3} \quad (\text{II.6.5a})$$

$$K_3 \propto \frac{k_B T}{D} c_P \quad (\text{II.6.5b})$$

In the semiflexible case K_1 is dominated by the one-particle contribution (II.3.7) which remains valid as long as the chains remain stretched [15]. When hairpins are present the situation changes as described in chapter IV.

II.7 Polyelectrolytes

In the preceding sections we only considered hard-core interactions, we will now include electrostatic repulsion for rods and semiflexible chains. When the polymers are charged (i.e. they are polyelectrolytes), there is an additional soft repulsion because of the electrostatic interaction between the polyelectrolytes and their surrounding double layers [3,27]. In the remainder of this chapter we closely follow the discussion of Stroobants et al. [27] for rods. Although the potential of mean force for two charged rods is in general very difficult to evaluate, we are helped by the fact that we need to know the Mayer function $[\exp(-w_{12}/k_B T) - 1]$, which is insensitive to the exact form of the potential when $w_{12}/k_B T \gg 1$. This implies that we only need to know an accurate form of the potential of mean force for configurations where only the outer parts of the double layers overlap. In the outer part of the double layer of a long rod the electric potential ψ^e always takes the Debye-Hückel form [28]

$$\frac{e\psi^e}{k_B T} \sim \Gamma K_0(\kappa r) \quad (\text{II.7.1})$$

where e is the elementary charge, r is the distance from the center line of the rod, κ^{-1} is the Debye screening length and K_0 is a modified Bessel function. Note that the proportionality constant Γ is determined also by the potential in the inner part of the double layer (which has to fulfil the nonlinear Poisson-

Boltzmann equation instead of its linearized Debye-Hückel version). Because a line charge with linear charge density ν_{eff} (i.e. number of charges per unit length) also gives a far-field form like eq. (II.7.1) [29]

$$\frac{e\psi^e}{k_B T} \sim 2\nu_{\text{eff}} Q K_0(\kappa r) \quad (\text{II.7.2})$$

it is possible to associate an effective line charge with our rod provided we choose

$$\nu_{\text{eff}} = \frac{\Gamma}{2Q} \quad (\text{II.7.3})$$

Q is the Bjerrum length $e^2/\epsilon k_B T$ with ϵ the dielectric permittivity. Because we argued that the contact between the outer parts of the double layers is dominant we can approximate w_{12} by the interaction between two effective line charges (at a shortest distance x and mutual angle γ) in the Debye-Hückel approximation, which is well-known [29-31]

$$\frac{w_{12}^e}{k_B T} = \frac{2\pi\nu_{\text{eff}}^2 Q e^{-\kappa x}}{\kappa \sin\gamma} = \frac{\pi\Gamma^2 e^{-\kappa x}}{2(\kappa Q) \sin\gamma} \equiv \frac{A' e^{-\kappa(x-D)}}{\sin\gamma} \quad (\text{II.7.4})$$

The last equality forms the definition of A' :

$$A' \equiv \frac{\pi\Gamma^2 e^{-\kappa D}}{2\kappa Q} \quad (\text{II.7.5})$$

Not surprisingly the potential of mean force (II.7.4) decays with the Debye length, while the factor $(\sin\gamma)^{-1}$ is proportional to the interaction area between the two crossed rods. Note that as a consequence of this last factor two charged rods tend to rotate to a perpendicular configuration.

To fix A' it is necessary to know Γ . For weakly charged polyelectrolytes this is simple because it is possible to use the Debye-Hückel approximation [32]

$$\frac{e\psi_{\text{DH}}^e}{k_B T} = \frac{4\nu Q K_0(\kappa r)}{\kappa D K_1(\kappa D/2)} \quad (\text{II.7.6})$$

valid if this does not exceed 1 for $r=D/2$. In (II.7.6) ν is the actual linear charge density and K_1 is here a modified Bessel function. Comparing (II.7.1) and (II.7.6) it is possible to derive a closed expression for A' from eq. (II.7.5) [27]

$$A'_{\text{DH}} = \frac{8\pi\nu^2 Q e^{-\kappa D}}{\kappa^3 D^2 K_1^2(\kappa D/2)} \quad (\text{II.7.7})$$

In two limits (thick and thin double layer) it is possible to simplify this with asymptotic expressions for $K_1(\kappa D/2)$ [33]

$$A'_{DH} \sim (2\nu^2 Q) \kappa^{-1} \quad (\kappa D \ll 1) \quad (\text{II.7.8a})$$

$$A'_{DH} \sim (8\nu^2 Q/D) \kappa^{-2} \quad (\kappa D \gg 1) \quad (\text{II.7.8b})$$

For more strongly charged polyelectrolytes it is necessary to solve the full Poisson-Boltzmann equation. In that case it is useful to employ the approximate analytical solution given by Philip and Wooding [28], from which Γ and A' are obtained by a simple numerical procedure.

With expression (II.7.4) for the potential of mean force it is possible to evaluate the cluster integral from eq. (II.1.12) [3]

$$\beta_1(\gamma) = -2L^2 D \sin \gamma + 2L^2 \sin \gamma \int_D^\infty [\exp(-w_{12}^e/k_B T) - 1] dx \quad (\text{II.7.9a})$$

$$\stackrel{(A' > 2)}{\simeq} -2L^2 D \sin \gamma - 2L^2 \kappa^{-1} \sin \gamma [\ln A' + C_E - \ln(\sin \gamma)] \quad (\text{II.7.9b})$$

with Euler's constant $C_E = 0.577215\dots$. Stroobants et al. [27] divided the effect of charge in two parts. The first becomes apparent when we determine the second virial coefficient in the isotropic state (eq. (II.1.11) with $f(\Omega) = 1/4\pi$)

$$B_2^{\text{iso}} = \frac{\pi}{4} L^2 D + \frac{\pi}{4} L^2 \kappa^{-1} [\ln A' + C_E + \ln 2 - 1/2] \quad (\text{II.7.10a})$$

$$= \frac{\pi}{4} L^2 \tilde{D} \quad (\text{II.7.10b})$$

indicating that in the isotropic state charge generates a larger effective diameter of the rods [3]

$$\tilde{D} = D \left[1 + \frac{\ln A' + C_E + \ln 2 - 1/2}{\kappa D} \right] \quad (\text{II.7.11})$$

The second effect is only present in the anisotropic state [27]

$$B_2^{\text{ani}} = \frac{\pi}{4} L^2 \tilde{D} [\rho(f) + h\eta(f)] \quad (\text{II.7.12})$$

with $\rho(f)$ defined by eq. (II.1.17). Apart from the larger effective diameter we see the second effect in the extra term

$$\eta(f) \equiv \frac{4}{\pi} \int f(\Omega) f(\Omega') [-\sin \gamma \ln(\sin \gamma) - (\ln 2 - 1/2) \sin \gamma] d\Omega d\Omega' \quad (\text{II.7.13})$$

which is called the twisting effect as it originates from the factor $(\sin \gamma)^{-1}$ in eq. (II.7.4). The relative importance of this effect is determined by the twisting parameter

$$h \equiv (\kappa \tilde{D})^{-1}$$

(II.7.14)

To illustrate the dependence of effective diameter $\tilde{D}$ and twisting parameter h on polyelectrolyte properties and salt concentration we give two representative examples in tables 1 and 2. As we might expect, $\tilde{D}$ increases with decreasing salt concentration (equivalent to increasing screening length κ^{-1}) and increasing charge density ν . For thin double layers ($\kappa D \gg 1$) the charge is completely screened and $\tilde{D}$ is nearly equal to D .

M	$\kappa^{-1}(\text{\AA})$	$\nu(\text{\AA}^{-1})$				
		1	0.4	0.2	0.1	0.04
0.001	96	27 (0.18)	26 (0.19)	24 (0.20)	21 (0.23)	13 (0.37)
0.003	56	15 (0.19)	14 (0.19)	13 (0.21)	11 (0.26)	6.2 (0.45)
0.01	30	8.0 (0.19)	7.6 (0.20)	6.7 (0.23)	5.2 (0.29)	-
0.03	17.6	4.8 (0.18)	4.4 (0.20)	3.8 (0.23)	2.8 (0.31)	-
0.1	9.6	2.9 (0.17)	2.6 (0.19)	2.1 (0.22)	-	-
0.3	5.6	2.0 (0.14)	1.7 (0.16)	1.5 (0.19)	-	-
1	3.0	1.5 (0.10)	1.3 (0.12)	-	-	-

Table 1 Ratio of effective and hard-core diameter $\tilde{D}/D$ and twisting parameter h (in brackets) as a function of ionic strength and linear charge density ν for a cylinder with $D = 20 \text{ \AA}$ in an aqueous solution at 25°C . Γ was determined from ref. 28. If no values are given, $A' < 2$.

M	$\kappa^{-1}(\text{\AA})$	$\nu(\text{\AA}^{-1})$				
		1	0.4	0.2	0.1	0.04
0.001	96	6.7 (0.14)	6.3 (0.15)	5.7 (0.17)	4.6 (0.21)	3.0 (0.32)
0.003	56	4.1 (0.13)	3.8 (0.15)	3.3 (0.17)	2.7 (0.21)	-
0.01	30	2.6 (0.12)	2.3 (0.13)	2.0 (0.15)	1.6 (0.19)	-
0.03	17.6	1.8 (0.10)	1.6 (0.11)	1.4 (0.12)	-	-
0.1	9.6	1.4 (0.07)	1.3 (0.08)	1.1 (0.09)	-	-
0.3	5.6	1.2 (0.05)	1.1 (0.05)	-	-	-
1	3.0	1.1 (0.03)	-	-	-	-

Table 2 The same as Table 1 for diameter $D = 100 \text{ \AA}$.

The variation of twisting parameter h is less easy to predict. From eqs. (II.7.11) and (II.7.14) we have

$$h = [\kappa D + \ln A' + 0.7703]^{-1} \quad (\text{II.7.15})$$

which is certainly small for thin double layers ($\kappa D \gg 1$). For large A' (usually implying thick double layers, $\kappa D \ll 1$) h would also be small, although in practice not as small as for thin double layers because of the logarithmic dependence on A' . An indication of the location of the maximum value of h can be acquired in the Debye-Hückel approximation. From eqs. (II.7.8) we see that the dependence of A' on κ^{-1} varies between a second and a first power:

$$A' \sim \kappa^{-\omega} \quad (1 \lesssim \omega \lesssim 2) \quad (\text{II.7.16})$$

Substituting in (II.7.15) and determining its maximum gives [27]

$$\kappa^{-1} \sim \frac{D}{\omega} \quad (\text{II.7.17})$$

which means we may expect a maximum for h for a Debye screening length on the order of the diameter. Apparently, this is also correct for table 1, although the Debye-Hückel approximation is not valid there. In practice, h will not be much larger than 0.5.

The total free energy for a solution of charged rods can be represented analogously to eq. (II.1.18) by use of eq. (II.7.12) [27]

$$\frac{\Delta F}{Nk_B T} = \text{cst} + \ln c_L + \sigma(f) + c_L[\rho(f) + h\eta(f)] \quad (\text{II.7.18})$$

with the number density ρ_L now scaled by the effective excluded volume (II.7.10b)

$$c_L \equiv \frac{\pi}{4} L^2 \tilde{D} \rho_L \quad (\text{II.7.19})$$

Stroobants et al. [27] determined the phase transition for this free energy. As scaled concentration (II.7.19) now takes the place of scaled concentration (II.1.15) the effect of the larger effective diameter is to shift the phase transition to lower volume fractions. On the other hand the anisotropic state is destabilized by the twisting effect. In chapter III we study the effect of charge on the elastic moduli for a solution of rodlike polyelectrolytes. For semiflexible polyelectrolytes in the limit ($L \gg P \gg \tilde{D}$) the two-particle interaction term will be the same as for rods to first order, which enables us to extend eq. (II.5.10) with the help of eq. (II.7.12). The resulting free energy is used to determine the phase transition for such systems in chapter V.

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[34] Sometimes the validity of the virial expansion eq. (II.1.10) [3] is questioned for the case of rods. Probably, this originates from a scrutiny of an expansion of the following term from the logarithm of the partition function

$$\ln\left[1 - \frac{N_L(N_L-1)}{V}B_2 + \dots\right] \simeq - \frac{N_L(N_L-1)}{V}B_2 \simeq -N_L\rho_L B_2 \quad (a)$$

which is certainly not valid for rods at the phase transition where $\rho_L B_2 \simeq \mathcal{O}(1)$ so $N_L\rho_L B_2 \gg 1$. It is illuminating to realize that Mayer and Mayer [1] already recognized this problem in the case of a monatomic gas and describe its solution by giving an alternative derivation without using eq. (a). The point is that the term in square brackets in (a) is itself the first term in an expansion of [35]

$$\left[1 - \frac{2B_2}{V}\right]^{\frac{N_L(N_L-1)}{2}} \simeq \exp\left[- \frac{N_L(N_L-1)}{V}B_2\right] \quad (b)$$

the logarithm of which is directly given by the right-hand side of eq. (a) without requiring $N_L\rho_L B_2 \ll 1$. This is the line Doi and Edwards [36] follow in their derivation of the free energy.

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CHAPTER III

ELASTIC MODULI OF A NEMATIC LIQUID-CRYSTALLINE SOLUTION OF POLYELECTROLYTES

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published in the Journal of Chemical Physics
87, 4223-4232 (1987)

III.0 Abstract

The elastic moduli of polyelectrolyte liquid crystals are calculated within the second virial approximation. A quantitative numerical and analytical theory is set up for rodlike polyelectrolytes in excess salt whereas qualitative relations are discussed for polyions under more general circumstances. Electrostatic interactions cause significant deviations from the usual hard rod interactions. The effective diameter increases, the persistence length increases as well and a torsional or twisting effect manifests itself because two polyion rods want to adopt a perpendicular orientation with respect to each other. In consequence, for rodlike polyelectrolytes the twist modulus depends only weakly on the macromolecular concentration whereas the bend modulus increases more strongly with concentration than it does for hard rods.

III.1 Introduction

During the past decade there has been a strong resurgent interest in liquid crystals that are primarily lyotropic. Work on the class consisting of polyelectrolyte molecules is also gradually gaining momentum. There are several reasons for this. Obtaining well-defined linear, semiflexible biopolymers is easier than making well-characterized synthetic macromolecules; but biopolymers generally carry charge in aqueous solution. Much is known about hard-core liquid crystals [1,2] although a great deal is not yet understood. However, our knowledge concerning systems with soft repulsions is meager at best. Studying the effect of electrostatic interactions, which, incidentally, are *always* screened because of the presence of counterions arising from the dissociation of the polyelectrolytes, is particularly useful because the screening or softness can be regulated precisely by varying the ionic strength. Moreover, our present-day understanding of nonlinearly screened electrostatics is virtually quantitative. Hence, definite predictions of the charge and ionic strength dependence of the properties of polyelectrolyte liquid crystals should be feasible. Lastly, charge and orientational order might conspire to yield new phenomena. For instance, we expect the usual electrohydrodynamic instabilities [3,4] to be markedly perturbed by phenomena intrinsic to polyelectrolyte solutions (the effect of electrical fields on polyelectrolytes is reviewed in ref. 6).

Recent experimental work on polyelectrolyte liquid crystals includes that on DNA [7-12], xanthan [10-12], tobacco mosaic virus (TMV) [13-16] and the potential polyelectrolyte schizophyllan [17-20]. Unfortunately, to date there has not been a concerted attempt at quantitatively assessing the effects of charge and ionic strength on the isotropic-to-nematic transition, elastic constants, order

parameters and so forth. From a theoretical point of view the electrostatic interactions can act in at least two ways: the hard-core diameter increases to a larger effective one and two probe polyions exert a twisting force on each other so that they favor perpendicular orientation. The latter is a nonnegligible effect particularly when the polyelectrolytes are weakly charged. Although Onsager [21] already hinted at this long ago, quantitative theories [22-24] of the influence of electrostatic interactions on the isotropic-to-nematic phase transition have appeared only recently. All this work, including ours, pertains to polyelectrolytes that are sufficiently charged (quantitatively, we must have $A' \geq 2$ in eq. (III.6)). After completing this article we became aware of recent Russian work [51], which indicates that for very weakly charged polyelectrolytes the effect of twist could be of interest at very low ionic strength.

Here, we calculate the elastic moduli for polyelectrolyte nematics by applying the analysis of refs. 22-24 to recent work on the moduli for the uncharged case [23,25,26]. Parenthetically, we note that the expressions derived by Grosberg and Zhestkov [25] are almost identical with those due to one of us [26] even though the methods of calculation are quite disparate (in the case of semiflexible chains). As one of us has explained in detail [24], all methods should ultimately agree.

It must be realized that our calculations suffer from inexorable restrictions. The work that is precise is valid for rods only; their length must not exceed the deflection length [24]. However, we do give simple qualitative expressions for semiflexible chains in the next section. As before we adopt the second virial approximation so that the theory for effectively rodlike polyelectrolytes can be regarded as quantitative if the effective aspect ratio (length divided by effective diameter) exceeds 100 and as semiquantitative if this ratio exceeds about 20. The electrostatic model used is standard in polyelectrolyte theory; its merits and deficiencies have been outlined at length in ref. 22 and references therein (also see section II.7 of this thesis). We have calculated the elastic moduli analytically within the Gaussian approximation which yields exact leading order terms. The analytical work provides not only physical insight but also a valuable check on the numerical analysis of the moduli. Lekkerkerker et al. [27] introduced a new numerical method of solving the Onsager integral equation, by writing the orientational distribution function as an exponential of a sum of Legendre polynomials. In this way we can get rid of one integration so that calculations become feasible on a personal computer. The method is easily adapted to the polyelectrolyte isotropic-nematic transition [22]; here we take it one step further to derive the elastic constants.

III.2 Qualitative Analysis for Highly Charged Polyelectrolytes

Before discussing the quantitative theory for rodlike polyelectrolytes we present some qualitative estimates of the moduli for several important limiting cases. Scaling analyses have been used extensively before by one of us [24,28-30]. The expressions given here are a simple generalization of earlier work.

We neglect the effect of twist - the dimensionless parameter h introduced in ref. 22 and in section II.7 must be small ($h \lesssim 0.1$). Hence, this section does not apply to weakly charged polyelectrolytes ($h \simeq 0.4$), even qualitatively.

A. Rodlike Polyions in Excess Electrolyte

The polyelectrolytes are dissolved in a 1-1 electrolyte solution of concentration n_s . The polyion number density is ρ_L . The electrostatic screening by the small ions is determined by the Debye length κ^{-1}

$$\kappa^2 = 8\pi Q n_s \quad (\text{III.2.1})$$

with Q the Bjerrum length

$$Q = \frac{q^2}{\epsilon k_B T} \quad (\text{III.2.2})$$

Here, q is the elementary charge, T the temperature, k_B Boltzmann's constant and ϵ the supposedly uniform permittivity of the solvent. For water at 25°C, $Q = 7.14 \text{ \AA}$ and $\kappa^{-1}(\text{\AA}) = 3.04 \times [n_s(\text{mol/l})]^{-1/2}$.

The charges on the polyion increase the hard-core diameter D to an effective one $\tilde{D}$. If $\kappa^{-1} \gg D$ then also $\tilde{D} \gg D$ and we have in fact [22]

$$\tilde{D} \simeq \kappa^{-1} \quad (\text{III.2.3})$$

In this section we delete all numerical coefficients and logarithmic terms. Since the twisting parameter h is much smaller than unity we can immediately derive the splay, twist and bend constants for the polyelectrolyte nematic by substituting $\tilde{D}$ for the diameter D in the eqs. of ref. 25 and 26 (we denote the elastic constants by primed variables; the corresponding unprimed variables are dimensionless and will be used in section III.4)

$$K'_1 = 3K'_2 \quad (\text{III.2.4})$$

$$K'_2 \simeq k_B T \tilde{D}^{-1} c_L \simeq k_B T L A_c \rho_A \quad (\text{III.2.5})$$

$$K'_3 \simeq k_B T \tilde{D}^{-1} c_L^3 \simeq k_B T L^3 A_c^3 \rho_A^3 n_s^{-1} Q^{-1} \quad (\text{III.2.6})$$

The usual scaled number density $c_L = (\pi/4) L^2 \tilde{D} \rho_L$ and the density of monomeric charges $\rho_A = (L/A_c) \rho_L$ where A_c is the contour distance between elementary charges viewed along the axis of a polyion.

There are several requirements on these expressions.

a) The second-virial approximation must hold [2,24]

$$\tilde{D} c_L L^{-1} \ll 1 \quad (\text{III.2.7})$$

b) The simple electrolyte is present in excess

$$n_s \gg \rho_A \quad (\text{III.2.8})$$

c) The rods must be rigid

$$L \lesssim \lambda \quad (\text{III.2.9})$$

The deflection length λ is proportional to the persistence length P and inversely proportional to the parameter α (defined in the next section) [28]. Near the rod limit α scales as c_L^2 [24]. Inequality (III.2.9) can be rewritten as

$$A_c^2 \tilde{D}^2 L^3 \rho_A^2 \lesssim P \quad (\text{III.2.10})$$

B. Rodlike Polyions without Electrolyte

Only the small ions from the polyelectrolyte determine the screening so that

$$\kappa^2 \simeq 4\pi A_c \rho_A \quad (\text{III.2.11})$$

where we have used the fact that when $A_c < Q$, a relation applicable to highly charged polyelectrolytes, only a fraction of the counterions is active in solution. Thus, eqs. (III.2.4) and (III.2.5) are unchanged whereas eq. (III.2.6) is modified

$$K'_3 \simeq k_B T L^3 A_c^2 \rho_A^2 \quad (\text{III.2.12})$$

Inequalities (III.2.7) and (III.2.10) must hold in this case also.

C. Semiflexible Polyelectrolytes with Excess Electrolyte

Let us assume the electrostatic persistence length [32]

$$P_{el} = \frac{1}{4Q\kappa^2} \quad (III.2.13)$$

is very small compared with P_0 , the intrinsic persistence length, although we insist on $\tilde{D} \simeq \kappa^{-1}$. As shown in refs. 24, 28 and 33 the scaled number density $c_P = (\pi/4)P^2\tilde{D}\rho_P$ with $\rho_P = (A/P)\rho_A$ replaces c_L as the relevant variable once the semiflexible chains are long enough ($L \gg \lambda$). Therefore, the extension of the expressions valid for uncharged polymers [25,26] becomes

$$K'_2 \simeq k_B T \tilde{D}^{-1} c_P^{1/3} \simeq k_B T (P_0 A_c Q n_s \rho_A)^{1/3} \quad (III.2.14)$$

$$K'_3 \simeq k_B T \tilde{D}^{-1} c_P \simeq k_B T P_0 A_c \rho_A \quad (III.2.15)$$

Inequality (III.2.8) must evidently be valid but eqs. (III.2.7) and (III.2.9) are changed to [24]

$$\tilde{D} c_P^{1/3} P_0^{-1} \ll 1 \quad (III.2.16)$$

$$L \gg \lambda \simeq P_0 c_P^{-1/3} \quad (III.2.17)$$

The splay constant K'_1 for semiflexible chains is not discussed here because there is controversy surrounding its calculation [25,26,34,35].

D. Polyelectrolytes without Salt

Let us assume eq. (III.2.13) is meaningful even without an excess of salt; we let $P_{el} \gg P_0$. Eqs. (III.2.3), (III.2.11) and (III.2.13-15) yield

$$K'_2 \simeq k_B T (A_c \rho_A / Q)^{1/3} \quad (III.2.18)$$

$$K'_3 \simeq k_B T / Q \quad (III.2.19)$$

Inequalities (III.2.16) and (III.2.17) must now be adhered to, with P_{el} replacing P_0 .

We now proceed to develop a quantitative theory for rodlike polyions in excess salt solution i.e. case A above. The relevance of our quantitative analysis to experiments will be discussed in the last section.

III.3 The Free Energy of the Nematic Phase

As in the previous section we consider a nematic phase consisting of N rodlike polyelectrolytes of length L and diameter D in a solvent (also containing an excess of 1-1 electrolyte). The total volume is V so that the number density of rods $\rho_L = N/V$. Besides a hard-core repulsion there will be an electrostatic repulsion between two test rods, which can be written approximately as [21,22]

$$\frac{w^{el}}{k_B T} = \frac{Ae^{-\kappa x}}{\sin \gamma} \quad (\text{III.3.1})$$

when their length L greatly exceeds both x, the shortest distance between the centerlines of the rods, and κ^{-1} , the Debye screening length. Furthermore, the polyions exert a twist on each other as signified by the $\sin^{-1} \gamma$ term with γ the angle between two test rods. The proportionality constant A depends on the polyelectrolyte properties in a complicated manner and is discussed at length by Stroobants et al. [22] (also see section II.7 of this thesis). Following Onsager [21] we introduce a single-rod orientational distribution function $f(\Omega)$ which is normalized:

$$\int f(\Omega) d\Omega = 1 \quad (\text{III.3.2})$$

The solid angle $\Omega = (\theta, \phi)$ where θ is the angle between the axis of a test rod and the director and ϕ is the azimuthal angle defined with respect to some reference axis. The 1-1 electrolyte is present in excess, so that counterions from the polyelectrolyte do not play a role in long range screening, i.e. polyion-small-ion interactions are neglected [43]. Hence, within the second virial approximation, the difference in Helmholtz free energy between the solution at hand and a pure salt solution in dialytic equilibrium is given by [21,22]

$$\begin{aligned} \frac{\Delta F}{Nk_B T} = & \frac{\mu^0}{k_B T} - 1 + \ln \rho_L + \int f(\Omega) \ln[4\pi f(\Omega)] d\Omega \\ & - \frac{\rho_L}{2V} \iiint \Phi(\mathbf{r}_2 - \mathbf{r}_1; \Omega_1, \Omega_2) f(\Omega_1) f(\Omega_2) d\Omega_1 d\Omega_2 d\mathbf{r}_1 d\mathbf{r}_2 \end{aligned} \quad (\text{III.3.3})$$

The reference chemical potential μ^0 is assumed to be independent of the ionic strength. The Mayer function Φ is defined as

$$\begin{aligned} \Phi = & -1 & (x \leq D) \\ = & \exp(-w^{el}/k_B T) - 1 & (x > D) \end{aligned} \quad (\text{III.3.4})$$

and consists of a hard-core and an electrostatic part. Onsager [21] defined cluster integrals, $\beta_1(\gamma) = \beta_1^{hc}(\gamma) + \beta_1^{el}(\gamma)$, by performing the $\mathbf{r}$ integrations in (III.3.3):

$$\beta_1^{hc}(\gamma) = \frac{1}{V} \iint \Phi^{hc}(\mathbf{r}_2 - \mathbf{r}_1; \Omega_1, \Omega_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (\text{III.3.5a})$$

$$= -2L^2 D \sin \gamma \quad (\text{III.3.5b})$$

and analogously

$$\beta_1^{el}(\gamma) = 2L^2 \sin \gamma \int_D^\infty [\exp(-w^{el}/k_B T) - 1] dx \quad (\text{III.3.5c})$$

$$= -2L^2 \kappa^{-1} \sin \gamma \left[\ln A' + C_E - \ln(\sin \gamma) + \mathcal{O}\left(\frac{\sin \gamma e^{-A'/\sin \gamma}}{A'}\right) \right] \quad (\text{III.3.5d})$$

with Euler's constant $C_E = 0.577215\dots$ and

$$A' = A \exp(-\kappa D) \quad (\text{III.3.6})$$

Expression (III.3.5d) holds for $A' \geq 2$ and applies to many practical situations. Note that the integration in (III.3.5c) starts at the point $x = D$ - where the rods touch each other - and that end effects are neglected as is justified for long rods. Finally we remark that expression (III.3.1) and thus (III.3.5d) too are not valid for very small angles $\gamma < D/L$, but these constitute only a small portion of the total range of possible angles and these configurations possess an unfavorable interaction energy. For this reason we can safely substitute eq. (III.3.5d) in eq. (III.3.3) for small angles. We also note that the theory is consistent because the typical values of γ in the nematic phase must be much larger than D/L if the second virial approximation is to hold (actually, this ratio should be $\tilde{D}/L$ - see eq. (III.3.10)).

Next, we write (III.3.3) in a more compact scaled form, the advantages of which have been dealt with in ref. [22].

$$\frac{\Delta F}{Nk_B T} = \frac{\mu^0}{k_B T} - 1 + \ln \rho_L + \sigma(f) + \tilde{b} \rho_L [\rho(f) + h\eta(f)] \quad (\text{III.3.7})$$

$\sigma(f)$ denotes the orientational entropic term:

$$\sigma(f) \equiv \langle \ln[4\pi f(\Omega)] \rangle \equiv \int f(\Omega) \ln[4\pi f(\Omega)] d\Omega \quad (\text{III.3.8})$$

$\rho(f)$ had been introduced for a pure hard-core interaction but is now related to an effective hard-core repulsion:

$$\rho(f) \equiv \frac{4}{\pi} \langle \sin \gamma \rangle \equiv \frac{4}{\pi} \iint f(\Omega_1) f(\Omega_2) \sin \gamma d\Omega_1 d\Omega_2 \quad (\text{III.3.9})$$

Thus, it is not multiplied by the usual isotropic excluded volume $b = (\pi/4)L^2 D$, but by one with D replaced by an effective diameter which was introduced by Onsager (but with a different A')

$$\tilde{D} = D \left[1 + \frac{\ln A' + C_E + \ln 2 - 1/2}{\kappa D} \right] \quad (\text{III.3.10})$$

Stroobants et al. [22] showed that in the anisotropic phase an additional aspect of the electrostatic interaction is important, as denoted by

$$\eta(f) \equiv \frac{4}{\pi} \langle -\sin\gamma \ln(\sin\gamma) \rangle - (\ln 2 - 1/2) \rho(f) \quad (\text{III.3.11})$$

which describes the tendency of two charged rods to twist away from a parallel configuration. The relative importance of this so-called twisting effect, which ultimately stems from the inverse power of $\sin\gamma$ in eq. (III.3.1), is determined by the twisting parameter [22]

$$h \equiv (\kappa \tilde{D})^{-1} \quad (\text{III.3.12})$$

We emphasize that this scaling or similarity transformation has effected the reduction of the number of relevant variables from five (L , ρ_L , D , κ and A') to two (h and the dimensionless concentration $c \equiv \tilde{b}\rho_L$).

The orientational distribution function $f(\Omega)$ is obtained by minimizing the free energy with respect to an arbitrary variation in the distribution. This leads to the integral equation

$$\ln[4\pi f(\Omega_1)] = E - \frac{8}{\pi} c \int \{1 + h[-\ln(\sin\gamma) - \ln 2 + 1/2]\} \sin\gamma f(\Omega_2) d\Omega_2 \quad (\text{III.3.13})$$

where the constant E is determined by applying the normalization condition (III.3.2). In this section we give both analytical and numerical methods for solving eqs. (III.3.7) and (III.3.13).

A. Analytical Approximation

In order to derive an analytical approximation we choose a simplified Gaussian form for $f(\Omega)$ [24-26]

$$\begin{aligned} g(\theta) &= \frac{\alpha}{4\pi} \exp(-\frac{1}{2}\alpha\theta^2) & (0 \leq \theta \leq \pi/2) \\ &= \frac{\alpha}{4\pi} \exp(-\frac{1}{2}\alpha(\pi-\theta)^2) & (\pi/2 \leq \theta \leq \pi) \end{aligned} \quad (\text{III.3.14})$$

which yields exact [26] leading terms for $\alpha \gg 1$. With regard to the free energy they are simply the first terms of previous expansions using the Onsager trial function [22]

$$\sigma(\alpha) \sim \ln \alpha - 1 \quad (\text{III.3.15})$$

$$\rho(\alpha) \sim 4\pi^{-1/2} \alpha^{-1/2} \quad (\text{III.3.16})$$

$$\eta(\alpha) \sim 2\pi^{-1/2} \alpha^{-1/2} (\ln \alpha - 2\ln 2 - 1 + C_E) \quad (\text{III.3.17})$$

To determine α we must minimize the free energy (III.3.7) with respect to α using the above expressions for $\sigma(\alpha)$, $\rho(\alpha)$ and $\eta(\alpha)$. Hence, we have

$$\alpha \sim 4\pi^{-1}c^2[1 + h(\frac{1}{2}\ln\alpha + \frac{1}{2}C_E - \ln 2 - \frac{3}{2})]^2 \quad (\text{III.3.18})$$

For $h = 0$ this leads to the usual Gaussian expression

$$\alpha(h=0) \sim 4\pi^{-1}c^2 \quad (\text{III.3.19})$$

The approximate iterative solution to eq. (III.3.18)

$$\alpha \simeq k_1 k_2^2 \ln^2\{k_2 \ln[k_2 \ln(k_2 \ln\{k_2 \ln k_2\})]\} \quad (\text{III.3.20})$$

with

$$k_1 \equiv \exp[3 + 2\ln 2 - C_E - 2h^{-1}]$$

and

$$k_2 \equiv 2h(\pi k_1)^{-1/2}c$$

is highly accurate, except when c is low and h is about 0.5 in which case it underestimates the exact α by a few percent. For small h eq. (III.3.20) reduces to the exact limiting relation

$$\alpha = 4\pi^{-1}c^2[1 + h(2\ln c + C_E - \ln \pi - 3)] \quad (h \rightarrow 0) \quad (\text{III.3.21})$$

Eq. (III.3.21) is accurate to within 2% for $h \simeq 0.1$.

B. Numerical Analysis

In order to calculate the distribution function $f(\Omega)$ numerically we use a method due to Lekkerkerker et al. [27,22]. We first expand $\sin\gamma$ and $-\sin\gamma\ln(\sin\gamma)$, appearing in eq. (III.3.13), in terms of Legendre polynomials

$$\sin\gamma = \sum_{n=0}^{\infty} c_{2n} P_{2n}(\cos\gamma) \quad (\text{III.3.22})$$

$$-\sin\gamma\ln(\sin\gamma) = \sum_{n=0}^{\infty} c'_{2n} P_{2n}(\cos\gamma) \quad (\text{III.3.23})$$

The coefficients c_{2n} are given by [36]

$$c_{2n} = - \frac{\pi(4n+1)(2n-3)!!(2n-1)!!}{2^{2n+2}n!(n+1)!} \quad n \geq 2 \quad (\text{III.3.24})$$

We have been able to find a general expression for c'_{2n} also:

$$c'_{2n} = c_{2n} \left[\ln 2 - \frac{5}{4} + \sum_{k=1}^{n-1} \left(\frac{1}{2(k+2)} + \frac{1}{2k-1} \right) \right] \quad n \geq 2 \quad (\text{III.3.25})$$

for $n = 0$ and $n = 1$ we have:

$$\begin{aligned} c_0 &= \pi/4, & c'_0 &= c_0[\ln 2 - 1/2] \\ c_2 &= -5\pi/32, & c'_2 &= c_2[\ln 2 - 5/4] \end{aligned} \quad (\text{III.3.26})$$

The entry for c'_{14} in table I of ref. 22 is incorrect. We substitute these expansions in the integral equation (III.3.13) and employ the addition theorem for Legendre polynomials [37]. This yields

$$f(\Omega) = f(\cos\theta) = Z^{-1} \exp \left[\sum_{n=0}^{\infty} \alpha_{2n} P_{2n}(\cos\theta) \right] \quad (\text{III.3.27})$$

where $Z = 4\pi e^{-E}$ is the normalization constant and the coefficients α_{2n} are given by the consistency relations

$$\alpha_{2n} = -\frac{8}{\pi} c \langle P_{2n} \rangle \{ c_{2n} + h[c'_{2n} - (\ln 2 - \frac{1}{2}) c_{2n}] \} \quad (\text{III.3.28})$$

where

$$\langle P_{2n} \rangle \equiv \int f(\cos\theta) P_{2n}(\cos\theta) d\Omega \quad (\text{III.3.29})$$

Because $f(\cos\theta)$ also appears in the calculation of $\langle P_{2n} \rangle$, eqs. (III.3.27) and (III.3.28) should be solved simultaneously. In practice we use only a limited number of terms ($n \leq k$) in the expansions (III.3.22) and (III.3.23), choose a set of starting values for α_{2n} ($n \leq k$) and iterate by repeatedly applying (III.3.27) and (III.3.28) in turn till a consistent set of α_{2n} ($n \leq k$) is reached, which gives us an n -parameter distribution function. We then add another polynomial to the Legendre expansion and use the above procedure again to see how much $f(\cos\theta)$ changes. When we are satisfied the coefficients α_{2n} have converged within chosen error bounds (above say $k = n_g$), we can use this solution of the distribution function to calculate properties of the liquid crystal like the different terms in the free energy (III.3.7), the order parameters and, as we shall see, the elastic constants. An estimate of how many Legendre polynomials should be taken into account to obtain convergence can be given by using their asymptotic behavior for large n [38]

$$P_{2n}(\cos\theta) \sim (\pi \sin\theta)^{-1/2} \cos[(2n+1/2)\theta - \pi/4] + O(n^{-3/2}) \quad (\text{III.3.30})$$

As can be seen from this expression P_{2n} is a highly oscillating function of θ . On the other hand, in the integrand of (III.3.29) it is multiplied by a sharply peaked distribution function. When the period of oscillation of P_{2n} namely

$(2\pi/(2n+1/2))$ is so small that the Legendre polynomial oscillates many times within the peak of the distribution function, the integral becomes very small. When we approximate the distribution function by eq. (III.3.14) (which works very well for the higher concentrations), we see that a measure of the peak width is $\alpha^{-1/2}$. These arguments give us a relation for n_g , the index beyond which we may truncate the Legendre expansion:

$$n_g \sim \alpha^{1/2} (=O(c)) \quad (\text{III.3.31})$$

In our numerical calculations we do indeed find such an approximate dependence of n_g on α : if our criterion for convergence is that two subsequent sets of α_{2n} should not differ by more than 0.1 % we find a proportionality constant of about 1.5 in the above relation between n_g and α .

In principle, the distribution function and the derived properties of the liquid crystal may now be determined numerically to arbitrary accuracy; in practice however, a problem arises for large n (≥ 16). For these values of n the coefficients of the corresponding Legendre polynomial, P_{2n} , become so large that they cannot be represented exactly even by double precision variables (this problem can be solved in principle but the following extrapolation method is sufficiently fast and accurate). This causes these polynomials to be increasingly inaccurate for higher n ; nevertheless, in view of eqs. (III.3.18) and (III.3.31), they will be needed for high c and h . One obvious way of dealing with this difficulty is to use eq. (III.3.30) or more detailed expansions. However, we circumvented it by calculating a series of values for each property, taking into account an extra Legendre polynomial every time. We then extrapolated the obtained series by noting that the differences between successive values decreased by a factor that varied only gradually. We checked this scheme by comparing our results with those of Herzfeld et al. [39], who calculated properties for uncharged rods according to the Onsager theory but via a numerical algorithm different from ours. As can be seen from table 1 our results do agree very well with those of ref. 39 up to a concentration of $c = 11.8$ but even at a concentration of 19.65 our calculations are within 1 % of theirs. This indicates that our results should be quite accurate even for very high values of α (about 500). We have also compared our numerical results for the nematic free energy at the isotropic to nematic transition for the charged rod fluid, with those of Stroobants et al. [22]. The results agree nicely except for the highest h values (which also implies higher c) in which case our values deviated by 3 % from theirs at most. This is due to the fact that they truncated the Legendre expansion beyond P_{14} , which is premature for the pertinent h and c values.

In conclusion, we can state that the expansion of the logarithm of the distribution function in Legendre polynomials is an efficient technique because one variable, the azimuthal angle ϕ , can be integrated out analytically. Moreover, once we know this expansion, other properties are readily computed as will be seen in the next section.

results	c	ρ	σ	$\langle P_2 \rangle$	$\langle P_4 \rangle$
Herzfeld et al.	19.63	0.1020	5.175	0.9937	0.9792
this work (num.)	19.63	0.1031	5.145	0.9932	0.9784
this work (anal.)	19.63	0.1019	5.196	0.9939	0.9796
Herzfeld et al.	11.78	0.1718	4.126	0.9819	0.9415
this work (num.)	11.78	0.1719	4.126	0.9819	0.9414
this work (anal.)	11.78	0.1698	4.175	0.9830	0.9434
Herzfeld et al.	7.85	0.2622	3.266	0.9578	0.8678
this work (num.)	7.85	0.2622	3.266	0.9577	0.8678
this work (anal.)	7.85	0.2546	3.364	0.9618	0.8727

Table 1 Comparison of our numerical and analytical results for uncharged rods with the numerical values of Herzfeld et al. [39].

III.4 Calculation of the Elastic Constants

We shall first derive an expression for the elastic constants very similar to the one Straley formulated [40] for a liquid crystal consisting of uncharged rods. In a distorted liquid crystal the director will not be constant but will depend on position. To a first approximation [41], the orientational distribution function will be the same as in the undistorted case provided that it is now peaked around the local director everywhere. Thus, the change in the free energy ΔF_d due to the implicit spatial variation of director $\mathbf{n}(\mathbf{r})$ is given by a generalization of eq. (III.3.3)

$$\Delta F_d = - \frac{1}{2} k_B T \rho_L^2 \iiint \Phi(\mathbf{r}_2 - \mathbf{r}_1; \Omega_1, \Omega_2) [f(\cos \theta_2(\mathbf{r}_2)) - f(\cos \theta_2(\mathbf{r}_1))] \times \\ f(\cos \theta_1(\mathbf{r}_1)) d\Omega_1 d\Omega_2 d\mathbf{r}_1 d\mathbf{r}_2 \quad (\text{III.4.1})$$

The orientational distribution is a function of $\cos \theta_i(\mathbf{r})$ where $\theta_i(\mathbf{r})$ ($i=1,2$) is now the space-dependent equivalent of θ_i of section III.3. This expression makes sense only if the inhomogeneity in the director is small enough, i.e. $L|\nabla \cdot \mathbf{n}(\mathbf{r})| \ll 1$. In addition, we assume the density of the solution remains uniform which is not true for the splay mode. Here, we simply neglect the term discussed by Meyer [35].

Eq. (III.4.1) is very similar to Straley's eq. (1) so we follow his analysis. In this way we come across a generalization of his eq. (5) pertaining to two arbitrary vectors $\mathbf{u}$ and $\mathbf{v}$

$$\begin{aligned}
 & - \int \Phi(\mathbf{r}_{12}; \Omega_1, \Omega_2) (\mathbf{r}_{12} \cdot \mathbf{u}) (\mathbf{r}_{12} \cdot \mathbf{v}) d\mathbf{r}_{12} \\
 & = \frac{1}{6} L^4 D' \{ (\mathbf{m}_1 \cdot \mathbf{u}) (\mathbf{m}_1 \cdot \mathbf{v}) + (\mathbf{m}_2 \cdot \mathbf{u}) (\mathbf{m}_2 \cdot \mathbf{v}) \} \sin \gamma [1 + \mathcal{O}(e^{-A'})] \\
 & + \frac{2}{3} L^2 D'^3 \{ (\mathbf{m}_1 \times \mathbf{m}_2) \cdot \mathbf{u} (\mathbf{m}_1 \times \mathbf{m}_2) \cdot \mathbf{v} \} \sin^{-1} \gamma \left[1 + \frac{\pi^2}{2(\kappa D')^2} - \frac{\psi''(1)}{(\kappa D')^3} + \mathcal{O}(e^{-A'}) \right]
 \end{aligned} \tag{III.4.2}$$

where $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$ and $\mathbf{m}_1$ and $\mathbf{m}_2$ are unit vectors aligned along two test rods (i.e. $|\mathbf{m}_1 \times \mathbf{m}_2| = \sin \gamma$).

$$D' = D \left[1 + \frac{\ln A' + C_E - \ln(\sin \gamma)}{\kappa D} \right] \tag{III.4.3a}$$

$$= \tilde{D} [1 + h(-\ln(\sin \gamma) - \ln 2 + 1/2)] \tag{III.4.3b}$$

and $\psi''(1) = -2.4041, \dots$. The second term of (III.4.2) may be neglected when

$$L/D' \gg 1 \tag{III.4.4a}$$

In view of the subsequent averaging over the distributions of both rods, this is equivalent to (cf. the discussion following eq. (III.3.6))

$$L/\tilde{D} \gg 1 \tag{III.4.4b}$$

This condition is in accord with the second virial approximation.

Next, we use eq. (III.4.1-3) together with arguments advanced by one of us [26] to obtain the following convenient expressions for the elastic moduli of nematic polyelectrolytes

$$K_i = - \frac{4c^2}{3\pi^2} \iint f'(\cos \theta_1) f'(\cos \theta_2) \sin \gamma [1 + h(-\ln(\sin \gamma) - \ln 2 + 1/2)] H_{i,0} d\Omega_1 d\Omega_2 \tag{III.4.5}$$

$$\text{Splay:} \quad H_{1,0} = 3H_{2,0} \tag{III.4.6}$$

$$\text{Twist:} \quad H_{2,0} = \frac{1}{4} \sin^2 \theta_1 (\cos \gamma - \cos \theta_1 \cos \theta_2) \tag{III.4.7a}$$

$$= \frac{1}{4} \sin^3 \theta_1 \sin \theta_2 \cos(\phi_1 - \phi_2) \tag{III.4.7b}$$

$$\text{Bend:} \quad H_{3,0} = \cos^2 \theta_1 (\cos \gamma - \cos \theta_1 \cos \theta_2) \tag{III.4.8a}$$

$$= \cos^2 \theta_1 \sin \theta_1 \sin \theta_2 \cos(\phi_1 - \phi_2) \tag{III.4.8b}$$

Here, K_i is K'_i scaled by $\tilde{D}/k_B T$ and c is ρ_L scaled by $\tilde{b} = (\pi/4)L^2\tilde{D}$. Note that $f'(\cos \theta)$ is the derivative of the distribution function with respect to its argument.

Moreover, we remark that the kernel appearing in the integral eq. (III.3.7) also occurs in the integrand of eq. (III.4.5) as could have been anticipated on intuitive grounds.

A. Analytical Approximations

We follow the lines of reasoning as developed in the case of pure hard-core interactions [26]. As our distribution function, $f(\cos\theta)$, we again use the Gaussian trial function (III.3.14), which is valid for large α . In that case the rods will be highly oriented and the distribution function will be very sharply peaked around the angles $\theta = 0$ and $\theta = \pi$. This means the predominant contribution to the integral (III.4.5) will originate from the region around these values of θ_1 and θ_2 , which implies that γ will also be near 0 or π . Therefore we may expand all functions in the integrand around these limits and the elastic constants will be given to lowest order by the following extensions of ref. 26.

$$K_2 \sim \frac{c^2}{6\pi^2} \alpha^2 \langle \gamma [1 + h(-\ln\gamma - \ln 2 + 1/2)] \theta_1^2 (\gamma^2 - \theta_1^2 - \theta_2^2) \rangle_0 \quad (\text{III.4.9})$$

$$K_3 \sim \frac{2c^2}{3\pi^2} \alpha^2 \langle \gamma [1 + h(-\ln\gamma - \ln 2 + 1/2)] (\gamma^2 - \theta_1^2 - \theta_2^2) \rangle_0 \quad (\text{III.4.10})$$

Here the Gaussian averages are defined as

$$\langle F(\theta_1, \theta_2, \gamma) \rangle_0 \equiv \iint F(\theta_1, \theta_2, \gamma) g(\theta_1) g(\theta_2) d\Omega_1 d\Omega_2 \quad (\text{III.4.11})$$

on the understanding that we use the complement of the angles θ_1 and θ_2 in the integrand whenever they occur within the interval $[\pi/2, \pi]$. Using the asymptotic values for the Gaussian averages as given in the appendix, we obtain

$$K_2 \sim \frac{7}{12} \pi^{-3/2} c^2 \alpha^{-1/2} [1 + h(Y - 1/7)] \quad (\text{III.4.12})$$

$$K_3 \sim \frac{2}{3} \pi^{-3/2} c^2 \alpha^{1/2} [1 + hY] \quad (\text{III.4.13})$$

$$(Y \equiv \frac{1}{2} \ln \alpha + \frac{1}{2} C_E - \ln 2 - \frac{3}{2})$$

These can be rewritten with the help of the Gaussian expression for α (III.3.18).

$$K_2 \sim \frac{7c}{24\pi} [1 - \frac{1}{7} h(1 + hY)^{-1}] \quad (\text{III.4.14})$$

$$K_3 \sim \frac{4c^3}{3\pi^2} [1 + hY]^2 \sim \frac{c}{3\pi} \alpha \quad (\text{III.4.15})$$

By combining these eqs. with the iterative solution for α (see eq. (III.3.18)) we

attain the Gaussian expression for the elastic constants. For $h = 0$ these formulas reduce to the Gaussian expressions for uncharged rods that one of us calculated previously [26].

Note that expressions (III.4.12) and (III.4.13) would have emerged as leading terms if we had used the Onsager trial function

$$f(\cos\theta) = \frac{\alpha \cosh(\alpha \cos\theta)}{4\pi \sinh\alpha} \quad (\text{III.4.16})$$

instead of the Gaussian (III.3.14), because the latter represents the leading behavior of the Onsager function for large α . We have also determined the next term in the asymptotic expansion of the elastic constants using the Onsager function, which is feasible though very laborious, by generalizing theorem (III.A.1) and taking derivatives with respect to α_1 and α_2 . However, this next term does not improve on (III.4.12) and (III.4.13) because of the form imposed on f in (III.4.16) (compare with fig. 1 of ref. 23).

B. Numerical Analysis

We will now sketch the numerical derivation of K_3 . Let us take equation (III.4.5) as our starting point together with expression (III.4.8b) for $H_{3,0}$. We substitute the Legendre expansions (III.3.22) and (III.3.23) for $\sin\gamma$ and $-\sin\gamma \ln(\sin\gamma)$ and apply the addition theorem [37] to each Legendre polynomial.

Now, the only dependence of the integrand upon azimuthal angles ϕ_1 and ϕ_2 pertaining to two probe rods is through the combination $\phi_1 - \phi_2$. We therefore transform one of the azimuthal integrations to an integration over $\phi_1 - \phi_2$. Because of the dependence of $H_{3,0}$ on $\cos(\phi_1 - \phi_2)$, only the $m=1$ term originating from the addition theorem remains, all other terms vanishing. The other azimuthal integration is trivial.

Next, the remaining double integral over $\cos\theta_1$ and $\cos\theta_2$ may be written as a sum of products of single integrals:

$$K_3 = -\frac{16}{3} c^2 \sum_{n=1}^{\infty} \frac{(2n-1)!}{(2n+1)!} [c_{2n} + h\{c'_{2n} + (-\ln 2 + 1/2)c_{2n}\}] I_1^n I_2^n \quad (\text{III.4.17})$$

where

$$I_1^n \equiv \int_{-1}^1 f(\cos\theta_1) P_{2n}^1(\cos\theta_1) \cos^2\theta_1 \sin\theta_1 d(\cos\theta_1) \quad (\text{III.4.18})$$

$$I_2^n \equiv \int_{-1}^1 f(\cos\theta_2) P_{2n}^1(\cos\theta_2) \sin\theta_2 d(\cos\theta_2) \quad (\text{III.4.19})$$

Lastly, since we have obtained the distribution function itself and not its derivative in section III.3, it is convenient to integrate (III.4.18) and (III.4.19) by parts. Furthermore, we can use several properties of associated Legendre functions [42] to rewrite these integrals:

$$I_1^n = - \int_{-1}^1 f(x) \left[(x^4 - x^2) \frac{d^2 P_{2n}}{dx^2} + (4x^3 - 2x) \frac{dP_{2n}}{dx} \right] dx \quad (\text{III.4.20a})$$

$$I_2^n = - \int_{-1}^1 f(x) \left[(x^2 - 1) \frac{d^2 P_{2n}}{dx^2} + 2x \frac{dP_{2n}}{dx} \right] dx \quad (\text{III.4.21a})$$

or after some exercise in recursion relations [53] for Legendre polynomials

$$I_1^n = - \frac{n(2n+1)}{\pi} \left[\frac{(2n+2)(2n+3)}{(4n+1)(4n+3)} \langle P_{2n+2} \rangle + \frac{(8n^2+4n-3)}{(4n-1)(4n+3)} \langle P_{2n} \rangle + \frac{(2n-2)(2n-1)}{(4n-1)(4n+1)} \langle P_{2n-2} \rangle \right] \quad (\text{III.4.20b})$$

$$I_2^n = - \frac{n(2n+1)}{\pi} \langle P_{2n} \rangle \quad (\text{III.4.21b})$$

Note that the $\langle P_{2n} \rangle$ are known from eq. (III.3.29).

A similar expression may be derived for the twist modulus:

$$K_2 = - \frac{4}{3} c^2 \sum_{n=1}^{\infty} \frac{(2n-1)!}{(2n+1)!} [c_{2n} + h(c_{2n}' + (-\ln 2 + 1/2) c_{2n})] I_2^n (I_2^n - I_1^n) \quad (\text{III.4.22})$$

The calculation of the distribution function and the elastic constants can be performed expediently on a personal computer (like the IBM PC-AT) because in the foregoing all multiple integrals have been reduced to single integrals. At the higher concentrations the values of the elastic constants did not converge completely with respect to the number of Legendre polynomials so we extrapolated them as described in the last part of section III.3. The results are given in tables 2 and 3.

We have compared our numerical results with those of Lee and Meyer [23] for uncharged rods. Our results are consistently somewhat lower than theirs (but the difference is at most 0.8 %). Note that our results did converge completely at these concentrations ($c < 7.5$), so this cannot be the reason for this difference. Furthermore we took great care in ensuring that we took enough steps in the discretization of the integrals.

In tables 2 and 3 we see that there is little effect of the charge density of the rods on the dimensionless splay and twist elastic constants (K_1 and K_2), whereas there is a strong influence on the bend elastic constant. For scaled concentrations smaller than 6 the bend elastic constant decreases with increasing h ; at $c \approx 6$, K_3 first increases and then decreases, though very slightly, and at higher concentrations it increases markedly with h . For the sake of completeness we also give the elastic constants at the concentrations of the isotropic-to-nematic phase transition in table 4 (concentrations as determined in ref. 22).

c	h	$K_2=1/3 K_1$	K_3
4.19	0.00	0.276	5.18
4.34	0.05	0.288	5.74
4.51	0.10	0.302	6.49
4.69	0.15	0.318	7.48
4.90	0.20	0.337	8.83
5.13	0.25	0.358	10.73
5.39	0.30	0.384	13.47
5.68	0.35	0.413	17.50
6.00	0.40	0.445	23.5
6.3	0.45	0.479	32.1
6.7	0.50	0.514	44.2

Table 4 *The elastic constants at the isotropic-to-nematic phase transition*

We now compare our analytical expressions, (III.4.14) and (III.4.15), with our numerical results. For that purpose we give the relative difference between them in table 5. As can be seen this relative difference decreases practically monotonically with increasing concentration as it should. We have also separated the effect of the electrostatic twist from that of the pure hard-core interaction by considering the quantity $(K_i - K_{i,0})/K_{i,0}$, where $K_{i,0}$ is the elastic constant for $h = 0$. The relative difference between analytical and numerical results for this quantity also decreases monotonically (see table 5).

We draw the conclusion that the Gaussian expressions (III.4.14) and (III.4.15) are fair to very good approximations to the numerically calculated elastic constants, becoming reliable at higher concentrations especially.

c \ h	0.00	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50
4.00	<i>3.940</i>	<i>3.418</i>	<i>2.795</i>	<i>1.991</i>							
5.00	11.73	11.37	10.97	10.50	9.94	9.26	8.43	7.35	5.86		
6.00	23.47	23.54	23.60	23.66	23.71	23.73	23.73	23.67	23.54	23.28	22.84
7.00	40.2	41.1	42.2	43.3	44.6	46.1	47.7	49.6	51.7	54.0	56.7
8.00	62.7	65.1	67.9	71.0	74.5	78.5	83.1	88.2	94.1	100.9	108.6
9.00	91.8	96.6	102.1	108.3	115.3	123.3	132.4	142.8	154.6	168.2	183.6
10.00	128.5	136.7	146.0	156.7	169	183	199	217	237	261	288
11.00	174	186	201	218	237	259	284	313	346	383	426
12.00	228	247	268	293	322	355	393	436	485	541	6.0 10 ²
13.00	292	318	349	385	426	473	527	588	6.6 10 ²	7.4 10 ²	8.3 10 ²

Table 2 Numerical values of the bend constant (K_3) for a polyelectrolyte nematic

The values in italics pertain to concentrations below the phase transition (and are thus metastable).
When there is no value stated, integral equation (III.3.13) has no solution, apart from the isotropic one.

c \ h	0.00	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50
4.00	<i>0.2452</i>	<i>0.2297</i>	<i>0.2088</i>	<i>0.1762</i>							
5.00	0.3832	0.3766	0.3692	0.3610	0.3514	0.3401	0.3260	0.3074	0.2795		
6.00	0.4933	0.4883	0.4831	0.4777	0.4721	0.4661	0.4598	0.4530	0.4455	0.4372	0.4276
7.00	0.595	0.590	0.586	0.581	0.576	0.571	0.567	0.562	0.558	0.553	0.549
8.00	0.694	0.688	0.683	0.679	0.674	0.669	0.665	0.661	0.658	0.654	0.651
9.00	0.790	0.784	0.779	0.774	0.769	0.764	0.760	0.756	0.753	0.750	0.747
10.00	0.886	0.879	0.873	0.868	0.862	0.858	0.853	0.850	0.846	0.844	0.841
11.00	0.980	0.973	0.967	0.961	0.955	0.950	0.946	0.942	0.939	0.936	0.934
12.00	1.074	1.067	1.060	1.053	1.047	1.042	1.037	1.034	1.030	1.028	1.026
13.00	1.169	1.160	1.153	1.146	1.140	1.134	1.13	1.13	1.12	1.12	1.12

Table 3 Numerical values of the twist constant ($K_2 = 1/3 K_1$) for a polyelectrolyte nematic

The values in italics pertain to concentrations below the phase transition (and are thus metastable).
When there is no value stated, integral equation (III.3.13) has no solution, apart from the isotropic one.

c \ h	in K_2						in K_3						in $(K_2 - K_{2,0})/K_{2,0}$			in $(K_3 - K_{3,0})/K_{3,0}$		
	0.0	0.1	0.2	0.3	0.4	0.5	0.0	0.1	0.2	0.3	0.4	0.5	0.1	0.3	0.5	0.1	0.3	0.5
5	21	24	28				44	48	55				-60			-40		
6	13	14	15	16	18		24	24	24	24	25		-31	-37		-70	-37	
7	9	9	10	10	11	11	15	14	12	11	9	8	-14	-17	-20	-27	-24	-21
8	7	7	7	7	8	8	10	9	7	5	4	2	-6	-7	-8	-20	-19	-18
9	6	6	6	6	6	6	7	6	4	2	1	-1	-3	-4	-3	-16	-16	-15
10	5	5	5	5	5	5	5	3	2	0	-1	-2	-3	-3	-2	-13	-13	-13
11	4	4	4	4	4	4	4	2	1	-1	-2	-3	-1	-2	0	-11	-11	-11
12	4	4	4	4	4	4	3	1	0	-2	-3	-4	-3	-4	0	-10	-10	-10
13	3	3	3	3	3	3	2	0	-1	-2	-3	-4	-1	-4	-1	-9	-9	-9

Table 5 The relative difference between the analytical and numerical values of the elastic constants (as a percentage of the respective numerical values)

III.5 Concluding Remarks

In order to gauge the consequences of the theory developed in sections III.3 and III.4 we illustrate a typical application.

Let us consider an aqueous solution of an intrinsically very stiff polyelectrolyte. We have in mind biopolymers like the fD virus or charged micelles whose properties are known beforehand. We suppose the particles are very slender with a contour length $L = 4000 \text{ \AA}$, a hard-core diameter $D = 50 \text{ \AA}$ and a persistence length P of order $10^5 \text{ \AA}$. The volume fraction of polyelectrolyte ϕ equals 0.04. A 1-1 electrolyte of concentration 0.003 M is also added to the solution; since the Bjerrum length $Q = 7.14 \text{ \AA}$ if the temperature is 298 K, the Debye length κ^{-1} is about $55.5 \text{ \AA}$ according to eq. (III.2.1).

Next, we suppose the linear charge density A_c^{-1} is 0.035 elementary charges per $\text{\AA}$. This is low enough for the validity of the Debye-Hückel approximation so that we may use eq. (II.7.7).

$$A' = \frac{8\pi Q e^{-\kappa D}}{A_c^2 \kappa^3 D^2 K_1^2(\frac{1}{2}\kappa D)} \quad (\text{III.5.1})$$

Here, K_1 is the first-order modified Bessel function of the second kind. In this example $A' = 1.71$ whence we calculate the effective diameter $\tilde{D} = 123 \text{ \AA}$ and twisting parameter $h = 0.453$ from eqs. (III.3.10) and (III.3.12). We can already conclude that the effect of twist must be substantial as expected for a weakly charged polyelectrolyte. The scaled concentration $c = \phi \tilde{D} L D^{-2} \approx 7.84$ is just above that at the transition. In view of table 5 the analytical approximations suffice so from eqs. (III.3.20) and (III.4.13) we get $\alpha = 113$ and $K_3 = 95$. In terms of measurable quantities $K_3' = k_B T \tilde{D}^{-1} K_3 = 3.2 \cdot 10^{-6}$ dynes. The influence of charge is marked: the more than twofold increase in effective diameter leads to a factor of 6 in the bend constant while the twisting effect provides an additional factor of 1.6. At this volume fraction, the corresponding system of uncharged rods is still isotropic.

This calculation exemplifies the way the various restrictions should be applied. Thus, the equivalent concentration $\rho_A = 4\phi/\pi D^2 A_c = 1.2 \cdot 10^{-3} \text{ M}$ is less than the concentration of electrolyte as it should be. Moreover, the second virial approximation ought to work reasonably well because $\alpha^{1/2} \ll L \tilde{D}^{-1}$ ($11 \ll 33$). In section III.2 we stated that the contour length must be smaller than the deflection length if the rigid-rod approximation is to hold. Eq. (IX.10) of ref. 24 (with $x_a = 0$) helps us make this statement more precise; the semiflexibility effect plays a minor role when

$$\frac{L\alpha}{6P} \lesssim 1 \quad (\text{III.5.2})$$

For the example at hand this expression equals 0.75 so the neglect of chain bending fluctuations is applicable although only just.

Experimental determination of the moduli for polyelectrolyte nematics conforming to the limitations of this chapter, has not yet been carried out. Some headway has been made for lyotropic liquid crystals consisting of poly- γ -benzyl-L-glutamate in various solvents [44-50]. We are not aware of any published work on polyelectrolytes except for that on tobacco mosaic virus by the Brandeis group [13,14,50] and on fD virus by Oldenbourg (as cited by Maret and Dransfeld [52]).

Unfortunately, TMV is not long enough for the second virial approximation to be accurate in any sense. But it might prove useful for qualitative purposes so let us see how far we get. In refs. 14 and 15 the volume fraction is about 0.16 and the ionic strength is apparently about 50 mM which together with a hard-core diameter $D = 180 \text{ \AA}$ and a linear charge density $A_c^{-1} \simeq 0.7 \text{ \AA}^{-1}$ lead to $A' = 22.3$, $\tilde{D} = 233 \text{ \AA}$ and $h = 0.058$ using the eqs. developed in ref. 22. The resulting c_a value of about 4 is too low to explain the order parameter $S \simeq 0.93$ [15] and the ratio $K_3/K_2 = 43$ [14]. But the two sets of measurements [14,15] can be rationalized for the S value implies a $\alpha \simeq 43$ so that eqs. (III.4.12) and (III.4.13) yield $K_3/K_2 \simeq 49$. The corresponding c value is 5.8. Presumably the relation between S and K_3/K_2 could be affected by the higher virial terms in a much lesser way than the relation between c_a and other quantities.

The second virial approximation is expected to work very well in the case of slender viruses. We have been able to find only one measurement by Oldenbourg [52] who obtained a K_2 of 10^{-8} dynes for an aqueous cholesteric solution of fD virus (concentration = 20 g/l; ionic strength = 0.01 M). The dimensions of such a rodlike particle are $D = 60 \text{ \AA}$ and $L = 8800 \text{ \AA}$. Assuming it is highly charged we have $\tilde{D} \simeq 200 \text{ \AA}$ and $h \simeq 0.15$. Letting the specific volume of the biopolymer have a reasonable value of 0.6 ml/g we estimate K_2 to be about $1.1 \cdot 10^{-8}$ dynes. Table III of ref. 22 predicts the onset of liquid crystal formation at 12 g/l compared with 11 g/l found experimentally [52]. Accordingly, both the twist modulus and the critical concentration are in accord with the electrostatic theory but clearly more data are needed if the theoretical analysis is to be put to a more stringent test.

Appendix

Here we elaborate a simple method developed by one of us for uncharged rods [26]. The Gaussian averages which are needed in eqs. (III.4.9) and (III.4.10) can be evaluated [26] by using the following theorem derived by Onsager [21]

$$\begin{aligned} J(\alpha_1, \alpha_2) &= \int \int \cosh(\alpha_1 \cos \theta_1 + \alpha_2 \cos \theta_2) F(\sin \gamma) d\Omega_1 d\Omega_2 \\ &= \frac{8\pi^2}{\alpha_1 \alpha_2} \int_{\gamma=0}^{\pi} \cosh(\alpha_1^2 + \alpha_2^2 + 2\alpha_1 \alpha_2 \cos \gamma)^{1/2} d[F(\sin \gamma)] \end{aligned} \quad (\text{III. A. 1})$$

Here, the function $F(\sin \gamma)$ must depend on $\sin \gamma$ only and $F(0) = 0$. The averages $\langle \gamma^p \rangle_0$ and $\langle \gamma^p \ln \gamma \rangle_0$ are obtained by choosing $F(x)$ to be x^p and $x^p \ln x$ respectively. For both choices we can make an asymptotic expansion for both forms of $J(\alpha_1, \alpha_2)$ given by eq. (III.A.1), using the properties of gamma- and psi-functions [42]. When we determine only the leading terms of the expansions we find the Gaussian averages:

$$\langle \gamma^p \rangle_{12} \sim \Gamma\left(\frac{p}{2} + 1\right) \left[\frac{2(a_1 + \alpha_2)}{\alpha_1 \alpha_2} \right]^{p/2} \quad (\text{III. A. 2})$$

$$\langle \gamma^p \ln \gamma \rangle_{12} \sim \Gamma\left(\frac{p}{2} + 1\right) \left[\frac{2(a_1 + \alpha_2)}{\alpha_1 \alpha_2} \right]^{p/2} \left[-\frac{1}{2} \ln \frac{\alpha_1 \alpha_2}{2(\alpha_1 + \alpha_2)} + \frac{1}{2} \psi\left(\frac{p}{2}\right) + \frac{1}{p} \right] \quad (\text{III. A. 3})$$

where the Gaussian average $\langle \dots \rangle_{12}$ is defined as in eq. (III.4.11) but with different α 's for the distribution functions of two test rods. The physically relevant averages $\langle \dots \rangle_0$ are obtained by taking $\alpha_1 = \alpha_2 = \alpha$. To obtain Gaussian averages of functions which also contain even powers of θ_1 or θ_2 we can use e.g.

$$\langle \theta_1^2 (\dots) \rangle_{12} = \frac{2}{\alpha_1} \langle \dots \rangle_{12} - 2 \frac{\partial}{\partial \alpha_1} \langle \dots \rangle_{12} \quad (\text{III. A. 4})$$

or

$$\langle (\theta_1^2 + \theta_2^2) \dots \rangle_0 = \frac{4}{\alpha} \langle \dots \rangle_0 - 2 \frac{\partial}{\partial \alpha} \langle \dots \rangle_0 \quad (\text{III. A. 5})$$

and elaborations.

We list the required averages below:

$$\begin{aligned} \langle \gamma^3 \rangle_0 &\sim 6\pi^{1/2} \alpha^{-3/2} \\ \langle \gamma(\theta_1^2 + \theta_2^2) \rangle_0 &\sim 5\pi^{1/2} \alpha^{-3/2} \\ \langle \gamma^3 \theta_1^2 \rangle_0 &\sim 21\pi^{1/2} \alpha^{-5/2} \\ \langle \gamma \theta_1^2 (\theta_1^2 + \theta_2^2) \rangle_0 &\sim \frac{35}{2} \pi^{1/2} \alpha^{-5/2} \end{aligned}$$

$$\begin{aligned}
\langle \gamma^3 (\ln \gamma) \rangle_0 &\sim (-3 \ln \alpha - 3C_E + 8) \pi^{1/2} \alpha^{-3/2} \\
\langle \gamma (\ln \gamma) (\theta_1^2 + \theta_2^2) \rangle_0 &\sim \left(-\frac{5}{2} \ln \alpha - \frac{5}{2} C_E + 6\right) \pi^{1/2} \alpha^{-3/2} \\
\langle \gamma^3 (\ln \gamma) \theta_1^2 \rangle_0 &\sim \left(-\frac{21}{2} \ln \alpha - \frac{21}{2} C_E + 31\right) \pi^{1/2} \alpha^{-5/2} \\
\langle \gamma (\ln \gamma) \theta_1^2 (\theta_1^2 + \theta_2^2) \rangle_0 &\sim \left(-\frac{35}{4} \ln \alpha - \frac{35}{4} C_E + \frac{47}{2}\right) \pi^{1/2} \alpha^{-5/2}
\end{aligned}$$

The terms without the logarithm were deduced previously [26].

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CHAPTER IV

THE INDUCED CHAIN RIGIDITY, THE SPLAY MODULUS AND OTHER PROPERTIES OF NEMATIC POLYMER LIQUID CRYSTALS

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published in *Macromolecules*
21, 2848-2858 (1988)

IV.0 Abstract

We present a numerical analysis of the induced chain rigidity or global persistence length, the order parameter, the splay modulus and other properties of a polymer nematic. The macromolecules are viewed as long slender wormlike cylinders interacting via hard-core repulsions in the second virial approximation. We calculate the orientational distribution function from the nonlinear integrodifferential equation first formulated by Khokhlov and Semenov. A bifurcation analysis of this equation is also given. Exact expressions for the susceptibility and the global persistence length are derived in terms of the distribution function. Analytical estimates of these quantities based on the usual methods are extremely poor approximations to those determined numerically. We also discuss the splay modulus which is directly related to the susceptibility and the global persistence length.

IV.1 Introduction

The average dimension of an *isolated* wormlike chain is a well-known function of the persistence length P which in turn equals the chain bending constant divided by the temperature [1,2]. It is not widely appreciated that this relation is not universally valid since it is statistical in nature. For instance when a semiflexible chain is strongly constrained to align more or less in one direction only, the usual persistence length P is no longer a relevant scale. Scaling and other types of analyses show that a new *local* scale emerges which may be called a deflection length λ [3,4]. This determines the statistical properties of a strongly confined worm e.g. its orientational free energy is proportional to the contour length divided by λ . In addition, there is also a second scale, the *global* persistence length g , which can be derived from λ by scaling arguments (see section IV.2). As its name implies, it is g that is related to the average dimension of a confined chain. As we shall see, the global persistence length governs various important quantities of the polymer nematic like the splay modulus.

The nematically induced *global* rigidity of a stiff chain has been the center of attention for some time [5-14]. However, most of the theory has been rudimentary with regard to the nature of the nematic field. Khokhlov and Semenov [6] did give a precise formulation of the global persistence length using a self-consistent field theory within the second virial approximation. Here, we note that there are in fact systems for which these approximations should work very well [4]. Nevertheless, Khokhlov and Semenov's WKB calculation of g is erroneous because their equation is strongly nonlinear so that the WKB

approximation is very poor.

This chapter has several aims. We first show that scaling arguments can be used to understand the connection between the global persistence length g , the splay modulus K_1 and the deflection length λ (section IV.2). Next, in order to set up a precise theory of these quantities we start by surveying the Khokhlov-Semenov integrodifferential equation (section IV.3). A bifurcation analysis of this is presented in section IV.4. We analyze the equation numerically (section IV.5), study the properties of the nematic phase (section IV.6) and compare the numerical analysis with the leading order solution (the so-called Gaussian approximation). For the sake of completeness we calculate the values of the thermodynamic quantities at the isotropic-nematic transition (section IV.7). In section IV.8 we derive an exact formula for the global persistence length in terms of the orientational distribution function and calculate g numerically using the information of the previous sections. Finally, we discuss the implications of our results in section IV.9.

IV.2 Qualitative Remarks

As we pointed out above, the deflection length λ is the scale of physical relevance in describing a strongly confined semiflexible chain. For a lyotropic nematic, λ is derived by qualitatively analyzing the correlation function $\langle \theta^2(|s-t|) \rangle$ for the angle $\theta(|s-t|)$ between two unit vectors tangential to the contour of the test chain at distances s and t from one end. For sufficiently small $|s-t|$ the orientational correlations should be in accord with the central limit theorem i.e. $\langle \theta^2(|s-t|) \rangle \approx |s-t|/P$ valid for a chain in dilute solution [2]. For larger distances the correlation function will eventually be restricted in view of the prevailing nematic order. Accordingly, we can identify a crossover distance $|s-t| = \lambda$ such that [3,4]

$$\langle \theta^2(|s-t|=\lambda) \rangle \approx \alpha^{-1} \quad (\text{IV.2.1})$$

$$\text{i.e.} \quad \lambda = P/\alpha \quad (\text{IV.2.2})$$

where the nematic order is specified by a parameter α ($\alpha \gg 1$; for a precise definition in terms of the orientational distribution function, see eq. (IV.6.5)).

A typical configuration of a nematically confined chain is depicted in fig. 1. The nematic field exerted by the surrounding chains deflects the test chain toward the director, about once every deflection length λ . However, if the chain is long enough there is a nonnegligible probability of the formation of hairpin bends, also shown in fig. 1. Since we postulate that λ is the sole relevant scale,

the contour length of such a sharp bend must be of order λ .

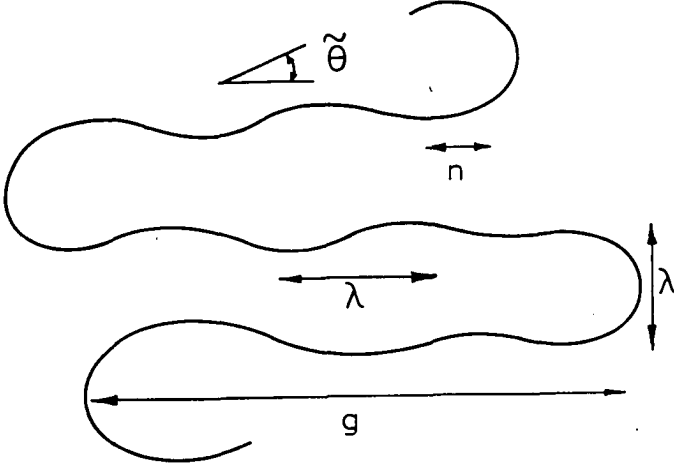


Fig. 1 A typical configuration of a very long semiflexible chain in the nematic field exerted by the surrounding polymer segments. There are two scales discernible: the deflection length λ and the global persistence length g . The orientational restriction is $\theta = \alpha^{-1/2}$ and the director is denoted by n .

The chain in fig. 1 is basically a one-dimensional random walk with fluctuating step length, its mean square extension R being given by a relation like

$$\langle R^2 \rangle \approx Lg \quad (L \gg g) \quad (\text{IV.2.3})$$

Here L is the contour length and the other factor must be the global persistence length g since g is proportional to an average step length. Thus, the distance between hairpin bends is also about g , on average [32]. Note that the U-turn bends or defects are actually distributed randomly along the chain contour. Hence, the statistical mechanical problem of calculating g boils down to an analysis of a one-dimensional gas of Lg^{-1} defects of concentration λg^{-1} (fluctuations in the step length can be disregarded).

The free energy of the defect gas in units of temperature T is simply

$$\frac{\Delta F_{\text{def}}}{k_B T} \approx \frac{L}{g} \ln\left(\frac{\lambda}{g}\right) + \frac{LP}{g\lambda} \quad (\text{IV.2.4})$$

One recognizes an ideal gas term and a bending energy per defect given by

$$U_{\text{bend}} = \frac{1}{2} P k_B T \int_0^\lambda \left[\frac{\partial \mathbf{v}}{\partial s} \right]^2 ds \approx P k_B T / \lambda \quad (\text{IV.2.5})$$

The inverse radius of curvature is $(\partial \mathbf{v} / \partial s)$ where $\mathbf{v}$ is the tangential unit vector at contour point s . Minimizing ΔF_{def} with respect to g yields

$$g \approx \lambda \exp(P/\lambda) \approx P \alpha^{-1} \exp(\alpha) \quad (\text{IV.2.6})$$

If the chains interact via excluded-volume interactions, the parameter $\alpha \approx c^{2/3}$ where the dimensionless variable c is the number density ρ_p of persistence segments scaled by the excluded volume $(\pi/4) P^2 D$ (P = persistence length, D =chain diameter)[3,4](see section IV.3). Hence, we have

$$g \approx P c^{-2/3} \exp(c^{2/3}) \quad (\text{IV.2.7})$$

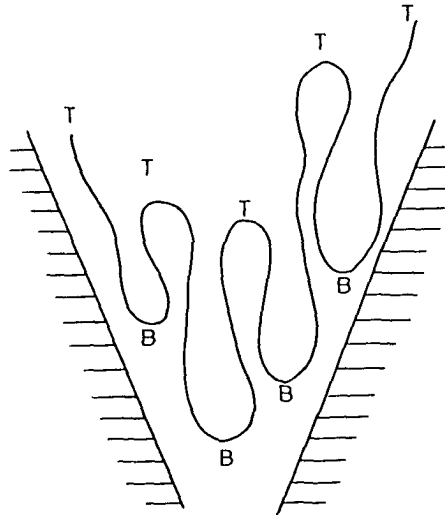


Fig. 2 The chain of fig. 1 under splay. The entropy of top (T) and bottom (B) hairpinlike bends is important.

Meyer [15] has shown that the splay modulus for nematic rigid rods is simply

$$K_1 \approx l^2 \rho_l k_B T \quad (\text{IV.2.8})$$

if their length is l and their number density ρ_l . If $L \gg g$ the solution of chains is effectively a solution of rods of length g because we want to count "end"

defects (see fig. 2). In view of the identity $l\rho_l = P\rho_p = g\rho_g$ we obtain

$$K_1 \approx gP\rho_p k_B T$$

$$\text{or } DK_1/k_B T \approx c^{1/3} \exp(c^{2/3}) \quad (\text{IV.2.9})$$

A precise theory of g and K_1 is developed in sections IV.8 and IV.9.

IV.3 Khokhlov-Semenov Integrodifferential Equation

Onsager's theory [16] on the formation of a nematic liquid crystal from a solution of long, slender molecules (length L , diameter D , persistence length P) is severely restricted by the requirement that the molecules have to be considered as completely rigid, thin rods ($P \gg L \gg D$). This is hardly ever fulfilled in nature. Khokhlov and Semenov [17] formulated a theory for very long, semiflexible molecules ($L \gg P \gg D$). Their expression for the free energy (here formulated as the free energy per persistence length segment, ΔF_p) as a functional of the orientational distribution function f can be written as

$$\frac{\Delta F_p}{k_B T} = \text{cst} + \sigma_p(f) + c\rho(f) \quad (\text{IV.3.1})$$

where the dimensionless variables σ , c and ρ are defined below.

Because, locally, the molecules can still be considered as almost fully rigid and rodlike, the second virial term $c\rho(f)$, which describes hard-core two-particle interactions (i.e. excluded-volume interactions), is identical to Onsager's, to a first approximation

$$\rho(f) \equiv \frac{4}{\pi} \int \int \sin \gamma f(\cos \theta) f(\cos \theta') d\Omega d\Omega' \quad (\text{IV.3.2})$$

By convention γ is chosen in such a way that $\sin \gamma \geq 0$. For very long chains f is the same for every infinitesimal chain section and θ is the angle between it and the director. The distribution is normalized

$$\int f(\cos \theta) d\Omega = 1 \quad (\text{IV.3.3})$$

The angle γ is that between two infinitesimal segments. If their orientations are described by polar angles (θ, ϕ) and (θ', ϕ') defined with respect to the director, then $\cos \gamma = \cos \theta \cos \theta' + \sin \theta \sin \theta' \cos(\phi' - \phi)$. $d\Omega \equiv d\cos \theta d\phi$ implies an integration over the full solid angle. The dimensionless concentration c signifies the number of persistence length segments present in a volume $b_p = (\pi/4) P^2 D$ (the isotropic excluded volume of two persistence length segments), i.e.

$$c \equiv \frac{\pi}{4} P^2 D \frac{L}{P} \rho_L \quad (\text{IV.3.4})$$

where ρ_L is the number density of the macromolecules.

Because of the semiflexibility of the chains, the expression [17] for the orientational entropy per persistence length is quite different from Onsager's for rods

$$\sigma_P(f) \equiv -\frac{1}{2} \int f^{1/2}(\cos\theta) \Delta f^{1/2}(\cos\theta) d\Omega \quad (\text{IV.3.5})$$

with

$$\Delta \equiv \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} = \frac{\partial}{\partial\cos\theta} (1-\cos^2\theta) \frac{\partial}{\partial\cos\theta} \quad (\text{IV.3.6})$$

i.e. the θ -dependent part of the Laplacian defined on a unit sphere. This expression is based on the wormlike chain model so it also takes into account the orientational fluctuations of a chain with respect to the director. The terms comprised in the constant, cst, are irrelevant to the rest of this article; it is important to note, however, that a translational entropy term which appears in Onsager's theory is negligible here because the persistence length segments are connected.

To find the distribution function $f(\cos\theta)$ we must minimize the free energy (IV.3.1) with respect to arbitrary variations in f . This leads to an integrodifferential equation

$$-\frac{1}{2}\Delta\psi^{-1}(\cos\theta) \Delta\psi(\cos\theta) = E - \frac{8c}{\pi} \int \sin\gamma \psi^2(\cos\theta') d\Omega' \quad (\text{IV.3.7})$$

where we plausibly define a "wave function" [4,17]

$$\psi(\cos\theta) \equiv f^{1/2}(\cos\theta) \quad (\text{IV.3.8})$$

E is a Lagrange multiplier originating from the constraint eq. (IV.3.3). Although eq. (IV.3.7) apparently involves a two-dimensional integration, it becomes an integrodifferential equation in one variable $\cos\theta$ ($=x$)

$$-\frac{1}{2}\Delta\psi(x) = \left[E - 16c \int_{-1}^1 S(x,x') \psi^2(x') dx' \right] \psi(x) \quad (\text{IV.3.9})$$

when we introduce the kernel $S(x,x')$ defined by

$$S(x,x') \equiv \frac{1}{2\pi} \int_0^{2\pi} \sin\gamma d\phi' \quad (\text{IV.3.10})$$

and $\Delta = \frac{\partial}{\partial x} (1-x^2) \frac{\partial}{\partial x}$ from now on.

IV.4 Bifurcation Analysis

As can be easily verified, eq. (IV.3.9) has an isotropic solution $\psi^i(x) = (4\pi)^{-1/2}$ for all values of c . Now the question arises whether an anisotropic solution is also feasible for certain values of c . Mathematically, we are dealing with a nonlinear operator equation with a variable parameter c . Thus, we turn to bifurcation theory which may tell us the concentration c^* at which a necessarily anisotropic solution branches off from the isotropic one. Kayser and Raveché [18] performed such an analysis on the integral equation for rigid rods, which has a different kind of nonlinearity though.

In our case we also need the Legendre expansion of the kernel $S(x, x')$ discussed in ref. 18, obtained by making a Legendre expansion of $\sin\gamma$ in terms of $P_{2n}(\cos\gamma)$ ($n = 0, 1, 2, \dots$), applying the addition theorem [19] and performing the ϕ' -integration in eq. (IV.3.10)

$$S(x, x') = \sum_{n=0}^{\infty} d_{2n} P_{2n}(x) P_{2n}(x') \quad (\text{IV.4.1})$$

with $d_0 = \pi/4$, $d_2 = -5\pi/32$ and

$$d_{2n} = - \frac{\pi(4n+1)(2n-3)!!(2n-1)!!}{2^{2n+2}n!(n+1)!} \quad n \geq 2 \quad (\text{IV.4.2})$$

Furthermore we should take into consideration that the Legendre polynomials are eigenfunctions of Δ

$$\Delta P_{2n}(x) = -2n(2n+1) P_{2n}(x) \quad (\text{IV.4.3})$$

Using these properties we show heuristically in appendix A that there is bifurcation at a scaled concentration $c^* = 6$ (as has been pointed out before [20]). Near this point at concentration

$$c = 6 + \nu \quad (\text{IV.4.4})$$

we argue that the integrodifferential equation has the following solution

$$\psi(x) = \frac{1}{\sqrt{4\pi}} [1 - \frac{7}{18}\nu P_2(x) + \mathcal{O}(\nu^2)] \quad (\text{IV.4.5})$$

obtained by combining eqs. (IV.A.9,10 and 15). Having thus ensured that the nematic state is feasible, we next turn to a numerical analysis of its properties.

IV.5 Numerical Procedure

We now want to find a numerical solution of eq. (IV.3.9). We have found it expedient to expand $\psi(x)$ in Legendre polynomials

$$\psi(x) = \frac{1}{\sqrt{4\pi}} \sum_{n=0}^{\infty} a_{2n} P_{2n}(x) \quad (\text{IV.5.1})$$

Because of the inversion symmetry of the nematic liquid crystal we retain the even polynomials only. Substituting (IV.5.1) in eq. (IV.3.9) and using eqs. (IV.4.1-3) result in

$$\sum_{n=0}^{\infty} n(2n+1) a_{2n} P_{2n}(x) = \left[E - \frac{8c}{\pi} \sum_{k,l,m=0}^{\infty} d_{2k} a_{2l} a_{2m} I_{2k,2l,2m} P_{2k}(x) \right] \sum_{n=0}^{\infty} a_{2n} P_{2n}(x) \quad (\text{IV.5.2})$$

Here $I_{k,l,m}$ represents the following integral

$$I_{k,l,m} \equiv \frac{1}{2} \int_{-1}^1 P_k(x) P_l(x) P_m(x) dx \quad (\text{IV.5.3})$$

and is explicitly given by [21]

$$I_{k,l,m} = \frac{(k+l-m)!(k-l+m)!(-k+l+m)!}{(k+l+m+1)!} \left[\frac{(\frac{k+l+m}{2})!}{(\frac{k+l-m}{2})!(\frac{k-l+m}{2})!(-\frac{k+l+m}{2})!} \right]^2 \quad (\text{IV.5.4})$$

provided $(k+l+m)$ is even and $(k+l-m)$, $(k-l+m)$ and $(-k+l+m)$ are never negative. In all other cases $I_{k,l,m} = 0$.

We now multiply (IV.5.2) by $P_{2j}(x)$ and integrate over x , using (IV.5.3) and the orthogonality of Legendre polynomials [19,21]. This yields

$$\frac{j(2j+1)}{(4j+1)} a_{2j} = \frac{E}{(4j+1)} a_{2j} - \frac{8c}{\pi} \sum_{k,l,m,n=0}^{\infty} d_{2k} a_{2l} a_{2m} a_{2n} I_{2k,2l,2m} I_{2k,2n,2j} \quad (\text{IV.5.5})$$

In this way the nonlinear integrodifferential equation (IV.3.9) has been transformed into an infinite set of nonlinear algebraic equations with as many unknown variables a_{2n} . Because E is unknown as well, we need an extra relation which follows from the normalization (IV.3.3)

$$\sum_{n=0}^{\infty} \frac{a_{2n}^2}{(4n+1)} = 1 \quad (\text{IV.5.6})$$

We now solve eqs. (IV.5.5-6) numerically by iteration, truncating the expansions at P_{2q} . Eq. (IV.5.6) is rearranged as

$$a_0^{(i)} = \left[1 - \sum_{n=1}^q \frac{a_{2n}^{(i)^2}}{(4n+1)} \right]^{1/2} \quad (\text{IV.5.7})$$

Eq. (IV.5.5) gives for $j=0$

$$E^{(i)} = \frac{8c}{a_0^{(i)}\pi} \sum_{k,l,m=0}^q \frac{d_{2k} a_{2k}^{(i)} a_{2l}^{(i)} a_{2m}^{(i)}}{(4k+1)} I_{2k,2l,2m} \quad (\text{IV.5.8})$$

where we have used the identity

$$I_{2k,2n,0} = \frac{1}{(4k+1)} \delta_{kn} \quad (\text{IV.5.9})$$

Finally, eq. (IV.5.5) yields for $1 \leq j \leq q$

$$a_{2j}^{(i')} = \frac{4j+1}{j(2j+1)} \left[\frac{E^{(i)}}{(4j+1)} a_{2j}^{(i)} - \frac{8c}{\pi} \sum_{k,l,m,n=0}^q d_{2k} a_{2k}^{(i)} a_{2l}^{(i)} a_{2m}^{(i)} a_{2n}^{(i)} I_{2k,2l,2m} I_{2k,2n,2j} \right] \quad (\text{IV.5.10})$$

The label (i) indicates the number of iterations made thus far.

For concentrations $c \leq 6$ the set of coefficients $a_{2j}^{(i')}$ obtained from eq. (IV.5.10) may be taken as the new set

$$a_{2j}^{(i+1)} = a_{2j}^{(i')} \quad (\text{IV.5.11a})$$

However, for higher concentrations this scheme turns out to be unstable. This problem is circumvented by tempering the change in the coefficients as for instance in the following way

$$a_{2j}^{(i+1)} = \frac{1}{c-4} a_{2j}^{(i')} + \frac{c-5}{c-4} a_{2j}^{(i)} \quad (\text{IV.5.11b})$$

We thus find a solution by choosing a set of starting values $a_{2j}^{(0)}$ ($1 \leq j \leq q$) and applying the above iteration scheme till the coefficients have converged to within chosen bounds. We then ascertain that the use of coefficients beyond q has a negligible effect.

Below a (scaled) concentration of 5.19 this iteration procedure yields only the isotropic solution, ψ^i ($a_0=1, a_2=a_4=\dots=0$). Between $c = 5.19$ and $c = 6$ however - depending on the choice of $a_{2j}^{(0)}$ - another solution is found, ψ^+ (with all $a_{2n} > 0$). Both the anisotropic and isotropic solutions are stable with respect to our iteration procedure i.e. when one of the coefficients is altered slightly the original solution is regained after iterating. Above the bifurcation point this is no longer true for the isotropic solution: a small perturbation does not die away. A small perturbation like $a_2^{(0)}=\epsilon, a_4^{(0)}=a_6^{(0)}=\dots=0$ with $\epsilon > 0$ iterates to the

anisotropic solution, ψ^+ . If $\epsilon < 0$ the iteration leads to a different kind of solution, ψ^- , with coefficients of alternating sign ($a_{4n} > 0$ and $a_{4n+2} < 0$). Choosing a random set of coefficients always results in one of the two anisotropic solutions ψ^+ and ψ^- if $c > 6$.

The combination of these results with those from the bifurcation analysis provides us with a clear picture of the stability diagram. For concentrations $c = 6 + \nu$ ($|\nu| \ll 1$) we expect a solution given by (IV.4.5). Our numerical solution ψ^- does indeed have $a_2 = -0.3888... \nu$ if ν is small enough and positive (coefficients higher than a_2 are negligible). For $\nu < 0$ the same kind of solution applies although it is unstable with respect to our iteration procedure. To illustrate the analysis graphically we plot a measure of the anisotropy of $\psi(x)$, viz. $N \equiv (1 - a_0)^{1/2}$, against c in fig. 3. This figure is similar to fig. 1 of ref. 18 which deals with the distribution function for entirely stiff rods (note that N is never greater than unity whereas the unbounded norm $\|(4\pi f - 1)\|$ in L_2 is used in ref. 18).

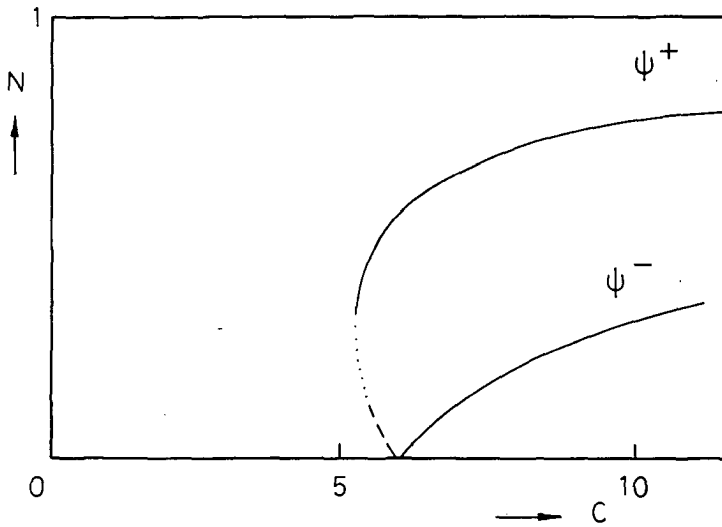


Fig. 3 Bifurcation diagram of the function $N = N[\psi] \equiv (1 - a_0^2)^{1/2}$ versus the concentration c . Solid curves denote the numerical solutions, the dashed line comes from the bifurcation analysis whereas the dotted line is interpolated. The lower solid curve represents the physically unrealizable state given by ψ^- .

Finally we elaborate some examples of our numerical procedure, focusing on ρ to estimate the degree of convergence. First we consider $c = 6$, in which case (IV.5.11a) can be used. Starting with $a_2^{(0)} = 1$, $a_0^{(0)} = a_4^{(0)} = \dots = a_{20}^{(0)} = 0$ we find that

the relative change per step in ρ is 1.10^{-6} after 20 iteration steps. The relative difference between the present value of ρ and the fully converged one (see the next section) is also about 1.10^{-6} . After 28 steps the relative change has decreased to 1.10^{-8} with a relative error of 5.10^{-9} . Thus for this concentration the procedure converges very fast. Taking all polynomials up to P_{40} into account gives the same values of the relevant properties. For $c = 20$ the numerical scheme converges much more slowly, mainly because we are forced to use (IV.5.11b). After 200 steps the relative change in ρ is 1.10^{-6} and the relative error 2.10^{-5} . These values are 1.10^{-8} and 2.10^{-7} resp. after 300 steps. Even here the difference between an expansion up to the fortieth degree and one up to the twentieth appears only in the tenth decimal for ρ and σ . We did not go beyond P_{40} in the expansion. This set an upper limit of about 50 for the concentration c .

IV.6 Properties of the Nematic Phase

Before we determine the properties of the nematic phase we first show to which anisotropic solution it corresponds. It is useful to focus on the order parameter

$$S \equiv 2\pi \int_{-1}^1 P_2(x) f(x) dx = \sum_{m,n=0}^{\infty} a_{2m} a_{2n} I_{2m,2n,2} \quad (\text{IV.6.1})$$

for the two solutions ψ^+ and ψ^- as a function of c (shown in fig. 4). The function ψ^+ has a positive order parameter and has maxima for $x = \pm 1$ ($\theta = 0$ or π). By contrast ψ^- has a negative order parameter, its only maximum being located at $x=0$ ($\theta=\pi/2$) so the molecules are more or less perpendicular to the director (note that in the plane perpendicular to the director the molecules are randomly oriented because we presuppose uniaxial symmetry). In order to assess the feasibility of ψ^+ and ψ^- we study the free energy $\sigma_P(f) + c\rho(f)$. From (IV.3.3,5,7 and 8) we derive

$$\sigma_P(f) = E - 2c\rho(f) \quad (\text{IV.6.2})$$

and from (IV.3.2 and 10) and (IV.4.1)

$$\rho(f) = \frac{4}{\pi} \sum_{k=0}^{\infty} d_{2k} \left[\sum_{l,m=0}^{\infty} a_{2l} a_{2m} I_{2k,2l,2m} \right]^2 \quad (\text{IV.6.3})$$

The free energy $\sigma_P(f) + c\rho(f)$ as a function of c is given in fig. 5. We see that the ψ^- state has a slightly lower free energy than the isotropic one but never lower than that pertaining to the ψ^+ state. The ψ^- state is physically irrelevant so we discard ψ^- altogether (note that it could be of use in more complex systems e.g. mixtures of chains and plates).

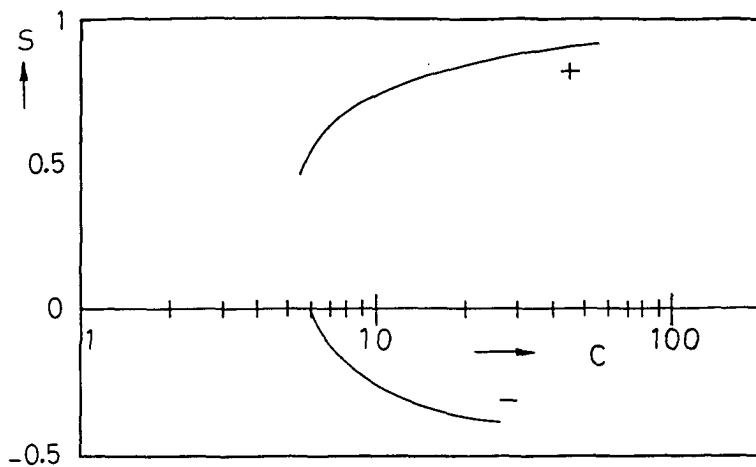


Fig. 4 The order parameter S of the two states ψ^+ (+) and ψ^- (-) versus the concentration c (on a logarithmic scale).

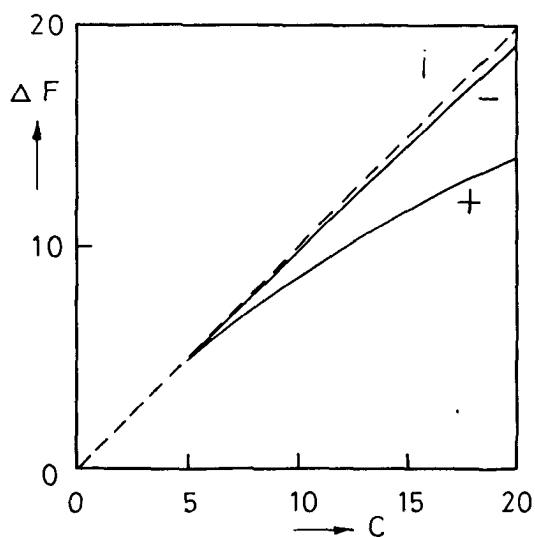


Fig. 5 The free energy ΔF of the isotropic (i) and the two nematic states (+) and (-) versus the concentration.

Before giving the numerical values we recall some previous analytical results. We use integrodifferential equation (IV.3.9) implicitly by choosing a trial function with a variational parameter (or parameters), calculating σ_P and ρ and minimizing the resulting expression for the free energy (IV.3.1) with respect to the parameter(s). Khokhlov and Semenov [17] chose the Onsager trial function [16]

$$f(\alpha) = \frac{\alpha}{4\pi} \frac{\cosh(\alpha \cos \theta)}{\sinh(\alpha)} \quad (\text{IV.6.4})$$

A simpler form of this trial function [4], the so-called Gaussian function, gives exact leading terms

$$\begin{aligned} f(\alpha) &= \frac{\alpha}{4\pi} \exp(-\frac{1}{2}\alpha\theta^2) & (0 \leq \theta < \pi/2) \\ &= \frac{\alpha}{4\pi} \exp(-\frac{1}{2}\alpha(\pi-\theta)^2) & (\pi/2 < \theta \leq \pi) \end{aligned} \quad (\text{IV.6.5})$$

This is borne out by inspection of eq. (IV.3.9). To leading order the free energy is calculated by making an asymptotic expansion of σ_P and ρ for large α using eq. (IV.6.5)

$$\sigma_P(\alpha) \sim \frac{\alpha}{4} \quad (\text{IV.6.6})$$

$$\rho(\alpha) \sim \frac{4}{\sqrt{\pi\alpha}} \quad (\text{IV.6.7})$$

Minimizing the resulting expression for ΔF_P with respect to α leads to the relation

$$\alpha \sim \frac{4c^{2/3}}{\pi^{1/3}} \quad (\text{IV.6.8})$$

A similar asymptotic expression for the order parameter can be found from the definition eq. (IV.6.1)

$$S(\alpha) \sim 1 - \frac{3}{\alpha} \quad (\text{IV.6.9})$$

In table I we give σ_P , ρ and S for different values of c and the relative difference compared with the leading terms of the analytical theory (note that it is better to focus on $1-S$ rather than S itself). We discern that $\sigma_P(\alpha)$ is not as good an approximation to the respective numerical values as $\rho(\alpha)$ and $S(\alpha)$ although the error term decreases nicely with increasing concentration. The Gaussian approximation of the excluded-volume term ρ works very well over the whole range of concentrations, though the error term changes sign at $c \approx 50$.

c	S	σ	ρ	$\frac{(1-S)-(1-S_G)}{1-S}$ (%)	$\frac{\sigma-\sigma_G}{\sigma}$ (%)	$\frac{\rho-\rho_G}{\rho}$ (%)
6	0.5448	1.030	0.8104	27	-119	7.3
8	0.6785	1.789	0.6996	15	-53	2.4
10	0.7358	2.313	0.6410	10	-37	1.1
12	0.7711	2.758	0.6003	8.4	-30	0.64
15	0.8062	3.356	0.5557	6.8	-24	0.36
20	0.8424	4.253	0.5040	5.4	-18	0.18
25	0.8654	5.069	0.4675	4.6	-15	0.10
30	0.8815	5.829	0.4398	4.0	-13	0.07
40	0.9029	7.230	0.3994	3.3	-10	0.03
50	0.9167	8.517	0.3706	2.8	-9	-0.02

Table 1 Numerical values of order parameter S , orientational entropy σ and excluded-volume parameter ρ for different concentrations. Further the relative difference between the numerical values and the Gaussian approximations, viz. $1 - S_G \sim 3/\alpha$, $\sigma_G \sim \alpha/4$ and $\rho_G \sim 4\pi^{-1/2}\alpha^{-1/2}$ as a function of concentration $c \sim \frac{1}{8}\pi^{1/2}\alpha^{3/2}$.

IV.7 The Isotropic-Nematic Phase Transition

To determine the isotropic-nematic phase transition we need to know the osmotic pressure (for a solution of volume V consisting of N macromolecules and a solvent of chemical potential μ_0)

$$\Pi = -\left.\frac{\partial \Delta F}{\partial V}\right|_{N, \mu_0, T} = \frac{k_B T}{b_P} c^2 \rho \quad (\text{IV.7.1})$$

and the chemical potential

$$\mu = \left.\frac{\partial \Delta F}{\partial N}\right|_{V, \mu_0, T} = \text{cst} + \frac{1}{P} k_B T [\sigma_P + 2c\rho] \quad (\text{IV.7.2})$$

At the phase transition the isotropic phase with concentration c_i , $\rho=1$ and $\sigma_P=0$ coexists with an anisotropic phase with concentration c_a , $\rho=\rho_a$ and $\sigma_P=\sigma_{P,a}$ at the same osmotic pressure and chemical potential. This leads to the coexistence equations

$$c_i^2 = c_a^2 \rho_a \quad (\text{IV.7.3})$$

$$2c_i = \sigma_{P,a} + 2c_a \rho_a \quad (\text{IV.7.4})$$

For the numerical calculation it is convenient to combine these two equations with eq. (IV.6.2), whence it follows that

$$c_a = \frac{E}{2\rho_a^{1/2}} \quad (\text{IV.7.5})$$

In order to analyze the phase transition numerically we pose an initial estimate of c_a and calculate the distribution function, E and ρ_a according to section IV.5 and eq. (IV.6.3). Then a revised estimate of c_a is obtained by substituting E and ρ_a into the right hand side of eq. (IV.7.5). We repeat this procedure until c_a does not change any more, eventually obtaining the following (scaled) quantities at the transition

$$\begin{aligned} c_i &= 5.1236 & c_a &= 5.5094 & S &= 0.46165 & \sigma_{P,a} &= 0.71761 & \rho_a &= 0.86484 \\ \Pi &= 26.25 \frac{k_B T}{b_P} & \mu &= \text{cst} + 10.25 \frac{L}{P} k_B T \end{aligned} \quad (\text{IV.7.6})$$

The expansion coefficients of the square root of the distribution function in the anisotropic phase are given in table 2 (cf. eq. (IV.5.1)). We also establish that the free energy of the anisotropic phase is $0.027 k_B T$ per persistence length lower than the corresponding isotropic of the same concentration.

a_0	0.878153980	a_{12}	$4.61598 \cdot 10^{-6}$
a_2	1.05936419	a_{14}	$2.50342 \cdot 10^{-7}$
a_4	$1.9825233 \cdot 10^{-1}$	a_{16}	$1.3123 \cdot 10^{-8}$
a_6	$1.9036052 \cdot 10^{-2}$	a_{18}	$6.688 \cdot 10^{-10}$
a_8	$1.337754 \cdot 10^{-3}$	a_{20}	$3.33 \cdot 10^{-11}$
a_{10}	$8.142318 \cdot 10^{-5}$		

Table 2 The Legendre coefficients a_{2n} of the function ψ at the I-N transition.

Let us compare our numerical results with those [4] obtained by using the Onsager trial function (IV.6.4)

$$c_i = 5.409 \quad c_a = 6.197 \quad S = 0.610 \quad \sigma_{P,a} = 1.376 \quad \rho_a = 0.762 \quad (\text{IV.7.7})$$

we see that eq. (IV.6.4) affords reasonable qualitative insight although it exaggerates the degree of anisotropy. The relative gap in concentration between the two phases as calculated numerically is much smaller than the one for

entirely stiff rods (for the numerical versions of Onsager's theory see [21,22])

$$\left. \frac{c_a - c_i}{c_i} \right|_{\text{flex}} = 0.075 \qquad \left. \frac{c_a - c_i}{c_i} \right|_{\text{rod}} = 0.274 \qquad (\text{IV.7.8})$$

The same applies to the order parameter

$$S_{\text{flex}} = 0.4617 \qquad S_{\text{rod}} = 0.792 \qquad (\text{IV.7.9})$$

IV.8 Global Persistence Length

As argued in section IV.2 the conformation of a nematically confined worm is essentially a one-dimensional random walk in the z direction (parallel to the director). Hence, if the contour length L is much larger than the global persistence length g , the mean-square extension of a test chain defines g in the usual way

$$\langle R_z^2 \rangle \equiv 2Lg \qquad (\text{IV.8.1})$$

We show below that this definition is consistent with the one valid for dilute solutions. It is generally recognized that the dimension of a polymer chain is connected with its susceptibility in analogy with other problems in statistical mechanics relating moments to correlation functions. Khokhlov and Semenov [6] stated the following relation without proof (for the sake of completeness we derive it in Appendix B)

$$\langle R_z^2 \rangle_0 = LP\chi_0 \qquad (\text{IV.8.2})$$

$$\text{with} \quad \chi_0 \equiv \left. \frac{\partial \langle P_1 \rangle}{\partial u} \right|_{u=0} = \frac{2g}{P} \qquad (\text{IV.8.3})$$

where the average is calculated for the nematic in an external field of the dipole type parallel to the director, i.e. an external free energy per persistence segment ΔF_{ext} is added to eq. (IV.3.1)

$$\frac{\Delta F_{\text{ext}}}{k_B T} = -u \int \cos\theta f(\cos\theta) d\Omega = -u \langle P_1 \rangle \qquad (\text{IV.8.4})$$

If a worm of length P were to be straightened out into a rod pointing in the z direction, its (dipole) energy would be $\pm uk_B T$ depending on its orientation.

In the remainder of this section, we focus on the dimensionless susceptibility χ_0 instead of g in view of eq. (IV.8.3). Upon minimizing the total

free energy consisting of the sum of eqs. (IV.3.1) and (IV.8.4) we get a more complex form of the original integrodifferential equation

$$-\frac{1}{2}\psi^{-1}(x) \Delta\psi(x) = E - 16c \int_{-1}^1 S(x, x') \psi^2(x') dx' + ux \quad (\text{IV.8.5})$$

To determine χ_0 we must solve (IV.8.5) for small u . Therefore we attempt a regular expansion in the small parameter u

$$\psi(x) = \psi_0(x) + u\psi_1(x) + \mathcal{O}(u^2) \quad (\text{IV.8.6})$$

where $\psi_0(x)$ is the solution of (IV.8.5) for $u=0$, which is symmetric in x . Because the applied field ux is antisymmetric, the first-order function $\psi_1(x)$ will be likewise. Using this property in expression (IV.A.1) we see that

$$E = E_0 + \mathcal{O}(u^2) \quad (\text{IV.8.7})$$

Substituting these expansions in eq. (IV.8.5) we find after retaining terms linear in u

$$\psi_0 \Delta\psi_1 - \psi_1 \Delta\psi_0 = -2x\psi_0^2 \quad (\text{IV.8.8})$$

It can be proved that a term originating from the integral vanishes as a consequence of the antisymmetry of ψ_1 .

We expect $\psi_1(x)$ to resemble $\psi_0(x)$ in some way which motivates the substitution

$$\psi_1(x) = h(x) \psi_0(x) \quad (\text{IV.8.9})$$

in eq. (IV.8.8). This gives a surprisingly simple differential equation for $h'(x)$

$$h''(x) + \left[2(\ln\psi_0)' - \frac{2x}{1-x^2} \right] h'(x) = - \frac{2x}{1-x^2} \quad (\text{IV.8.10})$$

It can be solved by standard analysis so that

$$\psi_1(x) = \psi_0(x) \int_0^x \frac{1}{(1-y^2) \psi_0^2(y)} \left[\int_y^1 2z\psi_0^2(z) dz \right] dy \quad (\text{IV.8.11})$$

where we have used the boundary condition $\psi_1(0) = 0$ and the fact that $\psi_1'(\pm 1)$ be finite.

To linear order in u we have

$$\langle P_1 \rangle = 4\pi u \int_{-1}^1 x \psi_0(x) \psi_1(x) dx + \mathcal{O}(u^2) \quad (\text{IV.8.12})$$

Applying the definition of the susceptibility in zero field (IV.8.3) and using expression (IV.8.11) for $\psi_1(x)$ we get an exact expression for χ_0 in terms of $\psi_0(x)$ after interchanging the order of the integrations

$$\chi_0 = 4\pi \int_0^1 \frac{1}{(1-y^2) \psi_0^2(y)} \left[\int_y^1 2x \psi_0^2(x) dx \right]^2 dy \quad (\text{IV.8.13})$$

Note that $\chi_0 = 2/3$ for the isotropic distribution, which is consistent with the usual expression for $\langle R_g^2 \rangle_0$ (see eq. (IV.8.2)).

Let us survey several seemingly plausible approximations to the susceptibility. The distribution is quite sharply peaked at $\theta=0$ and $\theta=\pi$. Hence, we can replace the term $\int_y^1 x f(x) dx$ by $\int_0^1 x f(x) dx$ in the integrand of eq. (IV.8.13), at least if we focus on the leading behavior of χ_0 only. Next, in view of the known asymptotic behavior of f toward the Gaussian $(4\pi)^{-1} \alpha \exp(\alpha(x-1))$ as x tends to unity, we attain an even more straightforward expression for the susceptibility valid for higher scaled concentrations c [25]

$$\chi_0 \sim \pi^{-1} \int_0^{1-\epsilon} [(1-x^2) f(x)]^{-1} dx \quad (\text{IV.8.14})$$

It is not so easy to simplify eq. (IV.8.14) further because we need to know more than merely the asymptotic behavior of f . Indeed, it is evident that a large contribution to χ_0 arises from the value of f near $x=0$. It turns out that a reliable estimate of χ_0 can be given only if we know f accurately in an appreciable range of x extending from zero. This necessitates analyzing eq. (IV.3.9) globally which no one has succeeded doing until now. A qualitative estimate can of course be obtained by the use of a trial function like eq. (IV.6.4). In that case eq. (IV.8.14) yields

$$\chi_0 \sim \pi \alpha^{-2} \exp(\alpha) \quad (\alpha \gg 1) \quad (\text{IV.8.15})$$

which should be compared with eq. (IV.2.6) ($\chi_0 = 2g/P$). It is also of interest to derive ψ_1 within the same approximation

$$\psi_1(x) \sim \psi_0(x) \left[\alpha^{-2} \exp(\alpha) \operatorname{arctg}(\sinh(\alpha x)) \right] \quad (\text{IV.8.16})$$

Accordingly, ψ_1 is essentially an antisymmetric version of ψ_0 multiplied by a large factor, except near $x=0$.

The susceptibility is rigorously obtained by integrating eq. (IV.8.13) numerically with the aid of the distribution derived in section IV.5. The

resulting χ_0 values are collected in table 3. We have checked these by another much more roundabout method because the numerical analysis of the markedly varying f is somewhat delicate. First, we solve eq. (IV.8.5) by the usual Legendre expansion of ψ and the kernel, not forgetting to incorporate the odd polynomials in ψ which arise because the symmetry is broken by the external dipole field. The iteration procedure is analogous to the one discussed in section IV.5. Finally, the susceptibility is calculated from eq. (IV.8.3) by determining $\langle P_1 \rangle$ for minute values of u . In the long run, this extremely slowly converging scheme yields the same values for χ_0 as before.

c	χ_0	c	χ_0
5.5094	6.506	13	1348.4
6	11.99	15	3948
7	29.51	18	$1.791 \cdot 10^4$
8	62.28	20	$4.642 \cdot 10^4$
9	123.34	25	$4.299 \cdot 10^5$
10	233.3	35	$2.28 \cdot 10^7$
11	428.1	50	$3.9 \cdot 10^9$
12	767.0		

Table 3 Numerical values of the susceptibility χ_0 as a function of the scaled concentration c . The lowest value of c represents the nematic at the I-N transition.

Inspired by the qualitative expressions eqs. (IV.2.6) and (IV.8.15) we have made least-squares fits of the numerical χ_0 versus the concentration according to

$$\chi_0 = c^{-2n/3} \exp(k_{n1}c^{2/3} + k_{n2} + k_{n3}c^{-2/3}) \quad n = 1,2 \quad (IV.8.17)$$

In order to accommodate all values of c , we have included a higher order term proportional to k_{n3} . This term is present since we know f can be expanded as

$$f \sim \frac{\alpha}{4\pi} \exp(-\frac{1}{2}\alpha\theta^2) [1 + d_1\theta^2 + d_2\theta^4 + \dots] \quad (IV.8.18)$$

The deviation of eq. (IV.8.17) from the numerical data of table 3 never exceeds about 5% for both values of n except for $c = 5.51$. Nevertheless, the physically motivated derivation of eq. (IV.2.6) is a better starting point than that leading to eq. (IV.8.15). For this reason and for the sake of definiteness we shall insist on setting n equal to unity in order to ease the comparison of qualitative theory

with our numerical analysis. We emphasize that the numerical values of χ_0 are described by some function $\exp[c^{2/3}m(c)]$ where $m(c)$ is slowly varying and unknown, so that the approximation eq. (IV.8.17) with $n=1$ is merely convenient and probably not imperative. The quality of the fit is shown in fig. 6; the constants are $k_{11} = 1.824$, $k_{12} = 0.705$ and $k_{13} = -10.18$. Using the asymptotic relation $\alpha \sim 4\pi^{-1/3}c^{2/3}$ we rewrite eq. (IV.8.17) as follows [31]

$$\chi_0 = 5.53 \alpha^{-1} \exp(0.668\alpha - 27.8\alpha^{-1}) \quad (\text{IV.8.19})$$

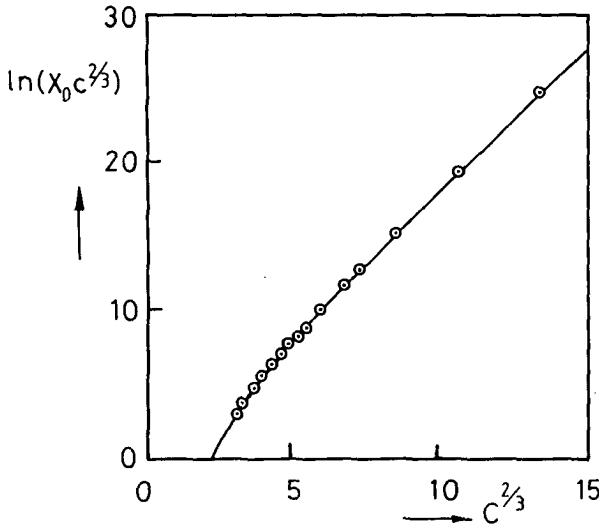


Fig. 6 Plot of $\ln(c^{2/3}\chi_0)$ versus $c^{2/3}$ obtained by a least-squares fit of $c^{2/3}\ln(c^{2/3}\chi_0)$ versus $k_{11}c^{4/3} + k_{12}c^{2/3} + k_{13}$ together with the numerical data.

IV.9 Discussion

The main analytical result of this chapter is eq. (IV.8.13), the susceptibility χ_0 or equivalently the global persistence length $g = \frac{1}{2}P\chi_0$ (eq. (IV.8.3)) expressed in terms of the distribution function $f(x) = f(\cos\theta) = \psi_0^2(\cos\theta)$. It may come as a surprise that eq. (IV.8.13) is valid not only for excluded-volume interactions (ρ

given by eq. (IV.3.2)) but for any interaction like

$$\rho_K(f) = \iint K(|\sin\gamma|) f(\cos\theta) f(\cos\theta') d\Omega d\Omega' \quad (\text{IV.9.1})$$

where the kernel K is quite general although it must of course allow for the existence of a state of uniaxial symmetry. In fact, if we minimize the total free energy of the system with $\rho_K(f)$ instead of $\rho(f)$ and in the presence of a slight dipolar field, we regain eq. (IV.8.8) on using $\psi \approx \psi_0 + u\psi_1$. Again, the cross term

$$\int_{-1}^1 \int_{-1}^1 \int_0^{2\pi} K(|\sin\gamma(\theta, \theta', \phi)|) \psi_0(\cos\theta) \psi_1(\cos\theta') d\cos\theta d\cos\theta' d\phi = 0 \quad (\text{IV.9.2})$$

since the integrand is antisymmetric under the transformation $(\theta, \theta', \phi) \rightarrow (\pi - \theta, \theta', \pi + \phi)$. Realistic examples of K include those pertaining to electrostatic and van der Waals interactions. We hope to come back to this topic in future contributions.

We have seen that the global persistence length is dominated by the behavior of f or ψ^2 near the equatorial region $x=0$ or $\theta=\frac{1}{2}\pi$. This behavior is not well known analytically so it is hard to deduce a reasonably accurate expression for χ_0 or g .

For a quantitative comparison of the computer results with analytical theory, we rewrite eq. (IV.8.19) in terms of the global persistence length

$$g = 2.77 P\alpha^{-1} \exp(0.688\alpha - 27.8\alpha^{-1}) \quad (\text{IV.9.3})$$

Qualitatively speaking, this is in agreement with the scaling analysis of section IV.2 for $\alpha \gg 1$. However, it is stressed again that the α^{-1} factor is not very meaningful. As we saw in the previous section the numerical data could have been rationalized just as easily by a different power law like α^{-2} instead of α^{-1} . Furthermore the bending energy of a hairpin may involve a term logarithmically dependent on α that would be neglected altogether in a scaling analysis. Of greater import is the predicted magnitude of χ_0 and g . At the I-N transition the global persistence length equals $3.25P$, whereas eq. (IV.2.6) yields about $100P$ and eq. (IV.8.15) about $50P$ (we have employed the value of $\alpha=6.5$ given in ref. 4). In practice the analytical estimates are useless. In fact, stiff polymers with contour lengths longer than about $10P$ are very difficult to deal with experimentally so that our predictions differ markedly from previous theories. The hopelessness of determining χ_0 by leading order approximations is in marked contrast with the success of calculating several other properties of the nematic state (see section IV.6).

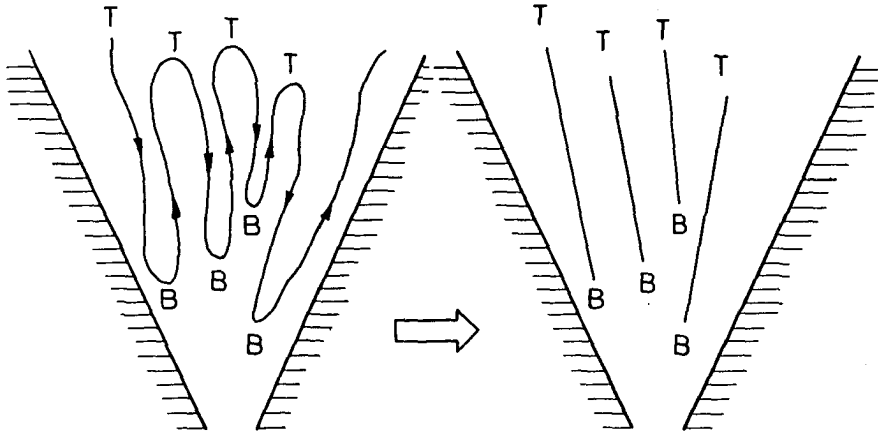


Fig. 7 A splayed nematic chain and its representation by effective rods. Chain sections pointing downwards are deleted.

The qualitative relation between g and the splay modulus K_1 discussed in section IV.2 can be made precise. Let us recall Meyer's result [15] for K_1 for a nematic solution of rods of length l and density ρ_l

$$K_1 = \frac{1}{4} l^2 \rho_l k_B T \quad (\text{IV.9.4})$$

Eq. (IV.9.4) is derived by assessing the inhomogeneity in the distribution of the top and bottom ends in a splayed nematic. When extending this expression to the case of semiflexible chains, we should bear in mind the following points. To an excellent approximation a nematic chain is a random walk along the director (when $\alpha \gg 1$); its statistical segment length A is twice the global persistence length. It is well known that the distribution of each step follows a Gaussian of zero mean and mean square equal to $A^2 = 4g^2$. Fig. 7 shows that in calculating the splay modulus we are to account for steps going in one direction only. Steps in the reverse direction are in effect redundant when we need specify merely the top and bottom ends of the effective rods of varying lengths l . It is readily shown that $\langle l \rangle = (2/\pi)^{1/2} g$ via the Gaussian distribution. Accordingly, we have

$$\begin{aligned}
K_1 &= \frac{1}{4}(2/\pi)^{1/2} g/\rho_l k_B T \\
&= \frac{1}{8}(2/\pi)^{1/2} \chi_0 P^2 \rho_P k_B T \quad (L \gg g) \quad (IV.9.5)
\end{aligned}$$

$$K_1 = \frac{1}{4} L^2 \rho_L k_B T \quad (L \ll g) \quad (IV.9.6)$$

As usual the index pertaining to the number density implies that we count the number of respective "segments". We rewrite eqs. (IV.9.5) and (IV.9.6) with the help of the relation $c = (\pi/4) P^2 D \rho_P$

$$\begin{aligned}
K_1 &= (2\pi^3)^{-1/2} \chi_0 c (k_B T/D) \quad (L \gg g) \quad (IV.9.7) \\
&= 0.257 c^{1/3} \exp(1.824 c^{2/3} - 10.18 c^{-2/3}) (k_B T/D)
\end{aligned}$$

$$K_1 = \pi^{-1} (L/P) c (k_B T/D) \quad (L \ll g) \quad (IV.9.8)$$

Eqs. (IV.9.7) and (IV.9.8) should be compared with the elastic moduli stemming from the excluded-volume effect [26,27]

$$\text{splay} \quad K_{1,ex} = 3K_2$$

$$\text{twist} \quad K_2 \approx c^{1/3} (k_B T/D) \quad (L \gg \lambda) \quad (IV.9.9)$$

$$\text{bend} \quad K_3 \approx c (k_B T/D) \quad (L \gg \lambda)$$

The splay modulus arising from the nonuniform distributions of "top" and "bottom" hairpins clearly overwhelms that caused by the excluded-volume effect: $K_1 \gg K_{1,ex}$. In general K_1 is also greater than K_2 . In practice, contour lengths are quite short (i.e. $L \ll g$ and $L = O(P)$) so that K_3 and K_1 are often of the same order of magnitude.

As is evident in the previous sections a fair part of our analysis is based on the work of Khokhlov and Semenov [6,17,20]. They were the first to formulate eq. (IV.8.5) and attempt its approximate solution. In their first method [6] they used a trial function akin to the usual ones showing that it led to an expression similar to eq. (IV.2.6) so this procedure is closely related to the scaling analysis of section IV.2. However, they rejected their first approach in favor of an analysis [6] inspired by Landau and Lifshitz's elegant treatment of quantum mechanical tunneling through a barrier [21]. Unfortunately, this analogy breaks down for two reasons. Eq. (IV.8.5) is strongly nonlinear so it is neither possible to employ a WKB approximation nor to consider an eigenfunction expansion of ψ in terms of a self-consistent field containing ψ itself. Comparison of our exact solution for the susceptibility (eq. (IV.8.13)) to their χ_0 bears out the disastrous effect of using methods devised for linear equations on highly nonlinear ones. Grosberg and Zhestkov [26] used the χ_0 of Khokhlov and Semenov [6] to calculate K_1 which explains why it is not in accord with eq. (IV.9.7).

Many analyses like that of ref. 13 are based on replacing the self-consistent field U_{scf} in eq. (IV.B.2) by $aP_2(\cos\theta)$ with a a constant. This replacement is ad hoc for several reasons. First, the nematic potential is much too strong to be described by an expansion valid for very weak order (order parameter $S \lesssim 0.1$). Second, the coupling of the environment to the test chain is utterly neglected. Furthermore, although the use of $U_{scf} \simeq aP_2(\cos\theta)$ leads to reasonably tractable equations [28], the complete self-consistent eq. (IV.8.5) can be solved exactly! Admittedly, the theory presented here is of the mean-field type but it is pointed out below that the influence of director fluctuations is negligible.

De Gennes [10] also presented an analysis for the global persistence length deriving

$$g = l \exp(\epsilon_h/k_B T) \quad (IV.9.10)$$

This treatment was meant for a chain wriggling in a nematic "matrix", l and ϵ_h being defined in terms of rather vaguely defined parameters B and Q ($=Q_0$): $l = (B/Q_0)^{1/2}$ and $\epsilon_h = 2(BQ_0)^{1/2}$. However, de Gennes' configurational free energy (his eq. (4)) turns out to be equivalent to that valid for a very long chain with excluded-volume interactions (see eq. (VIII.19) of ref. 4) provided we identify Q_0 and B as follows: $Q_0 \rightarrow k_B T \alpha^2 / 4P$, $B \rightarrow P k_B T$. Hence we have $l = 2\lambda$ and $\epsilon_h = \alpha k_B T$ so that eq. (IV.9.10) scales as eq. (IV.2.6). This equivalence is another example of the variety of ways of analyzing confined semiflexible chains [4]. Again, eq. (IV.9.10) overestimates eq. (IV.8.15) by more than an order of magnitude at the very least, so this type of theory is of very little use in predicting the outcome of experiments.

The appendix to ref. 10 proves useful in elucidating the import of director fluctuations. They cause a renormalization of the original Q_0 ($=\alpha^2 k_B T / 4P$ in our case; with neglect of fluctuations) to an effective one given by $Q_{eff}^{-1} = Q_0^{-1} + Q_1^{-1}$. An analysis of the effect of a configuration of a test chain on the surrounding nematic shows that $Q_1 = K / \ln(qD)^{-1}$ when the wavevector of the chain undulation is of magnitude q . The hybrid modulus K is some complicated function of K_1 , K_2 and K_3 (eqs. (IV.9.7-9)). We may set $q \simeq \lambda^{-1} \simeq \alpha/P$ in our case so that

$$\begin{aligned} Q_1/Q_0 &\simeq PD^{-1}\alpha^{-3/2}\exp(m\alpha) & (L \gg g) & \text{splay} \\ Q_1/Q_0 &\simeq PD^{-1}\alpha^{-3/2}(L\alpha/P) & (L \ll g) & \text{splay} \\ Q_1/Q_0 &\simeq PD^{-1}\alpha^{-3/2} & & \text{twist} \\ Q_1/Q_0 &\simeq PD^{-1}\alpha^{-1/2} & & \text{bend} \end{aligned} \quad (IV.9.11)$$

if we consider each pure deformation separately. Our analysis holds in the

second virial approximation i.e. $D/\lambda \ll \alpha^{-1/2}$ or $P/D \gg \alpha^{3/2}$. Accordingly Q_1/Q_0 is much larger than unity so Q_0 need not be renormalized thus justifying the neglect of fluctuations.

We have not been able to find any experimental data with which we can compare our theory. In general the lyotropic polymers used are too short. There is an interesting useful Monte Carlo simulation of the global stiffening of a semiflexible chain as it enters the nematic phase [8]. Khalatur et al. have determined the ratio of the respective mean square extensions $\langle R^2 \rangle$ in the nematic and isotropic phases. From its value of 1.13 we can calculate $g \approx 1.5P$ on employing the usual formula for $\langle R^2 \rangle$ as a function of the contour length ($L \approx 1.34P$ [8]) and persistence length. Because the contour length is still rather short, we cannot use c_a (eq. (IV.7.6)). Now it stands to reason that g and S are very well correlated. Thus we use Khalatur's estimate for the order parameter $S = 0.37 \pm 0.05$ [8], from which we determine numerically $c_a = 5.26 \pm 0.06$ and $\chi_0 = 3.8 \pm 1$ or $g = (1.9 \pm 0.5)P$. Hence, this Monte Carlo result agrees reasonably well with theory although the comparison must be viewed as tentative for now.

Finally, we discuss the experimental implications of our results. The numerical calculations of sections IV.5 and IV.6 can be used for sufficiently stiff polymers ($P/D \gg \alpha^{3/2}$) that are long enough ($L \gg \lambda$) provided dispersion forces are very weak. The conditions for the validity of the quantities pertaining to the isotropic-nematic transition (section IV.7) are somewhat more stringent ($L \gg P$). The Gaussian approximation works much better than expected. Accordingly, previous work on the moduli [26,27], the pitch of cholesterics [29] and the surface tension [30] ought to have a reasonably wide range of validity. The calculation of these quantities for arbitrary contour lengths is in general very tedious even in the Gaussian approximation. The only useful result that has been attained is for the order parameter [4]

$$S \sim 1 - 3/\alpha(L) \quad (\text{IV.9.12})$$

with $\alpha(L)$ implicitly given by

$$\alpha^{1/2} [1 + (L\alpha/6P)(1 + \frac{1}{2}\tanh(\alpha L/5P))] = 2\pi^{-1/2}(Lc/P) \quad (\text{IV.9.13})$$

No experimental assessment of this expression has been published. Numerical work for all contour lengths is sorely needed especially of the variables at the phase transition.

The dependence of the global persistence length g on the concentration is spectacular so it should be readily discernible under the right circumstances. Table 3 shows that g has a lower bound equal to $3.25P$. If one wants to test the theory of induced rigidity, one should choose chains with a contour length larger than $3.25P$ and measure the splay modulus at and just above the isotropic-

nematic transition. As the concentration increases, K_1 should increase very rapidly until it saturates when g has reached the contour length (fig. 8).

Acknowledgement

One of us (G.J.V.) thanks Profs. L.A. Peletier and Ph.P.J.E. Clément for discussions concerning subtleties involving the bifurcation analysis.

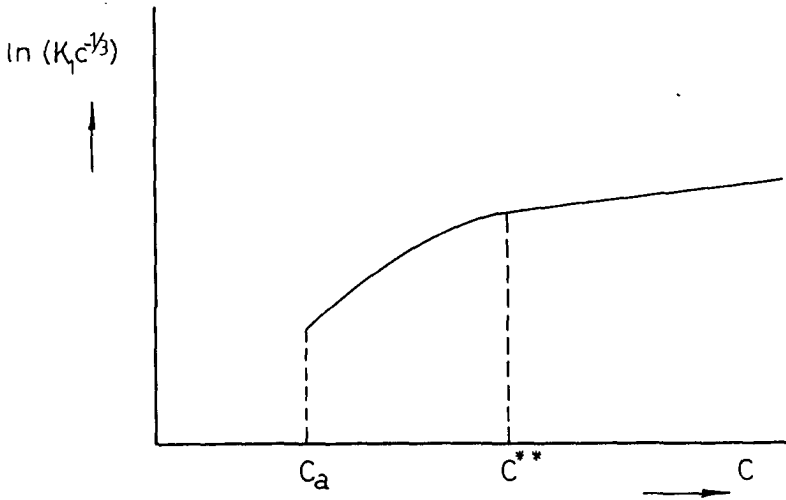


Fig. 8 Plot of the logarithm of the splay modulus K_1 times $c^{-1/3}$ versus the concentration c when the chain contour L is appreciably longer than the global persistence length g at the I-N transition c_a . Note that $g \approx L$ at $c \approx c^{**}$ where c^{**} denotes a crossover concentration.

Appendix A

We perform a bifurcation analysis of eq. (IV.3.9). First we must find an expression for the Lagrange multiplier E in terms of $\psi(x)$. We divide eq. (IV.3.9) by $\psi(x)$ and integrate over x , using the normalization condition (IV.3.3), the kernel expansion (IV.4.1) and the orthogonality properties of Legendre

polynomials. In this way we obtain

$$E = 2c - \frac{1}{4} \int_{-1}^1 \psi^{-1}(x') \Delta \psi(x') dx' \quad (\text{IV.A.1})$$

Defining the operator

$$\begin{aligned} F(\psi, c) \equiv & \frac{1}{2} \Delta \psi(x) - \frac{1}{4} \psi(x) \int_{-1}^1 \psi^{-1}(x') \Delta \psi(x') dx' \\ & + 2c \psi(x) \left[1 - 8 \int_{-1}^1 S(x, x') \psi^2(x') dx' \right] \end{aligned} \quad (\text{IV.A.2})$$

we are posed with the problem of solving the operator equation

$$F(\psi, c) = 0 \quad (\text{IV.A.3})$$

The bifurcation analysis determines the concentration c^* at which a new solution branches off from the isotropic one

$$\psi^1(x) = \frac{1}{\sqrt{4\pi}} \quad (\text{IV.A.4})$$

From now on we follow the line of reasoning of ref. 24 to determine the bifurcation point. Accordingly we look for nontrivial solutions $\phi(x)$ and the corresponding concentrations c^* of the branching equation

$$D_1 F\left(\frac{1}{\sqrt{4\pi}}, c^*\right) \cdot \phi = 0 \quad (\text{IV.A.5})$$

where we introduce an appropriate Banach space and take the Fréchet derivative $D_1 F(1/\sqrt{4\pi}, c)$ of operator (IV.A.2) with respect to ψ at the "point" $1/\sqrt{4\pi}$ in this Banach space [33]. In this case

$$D_1 F\left(\frac{1}{\sqrt{4\pi}}, c\right) \cdot \phi(x) = \frac{1}{2} \Delta \phi(x) - \frac{1}{4} \int_{-1}^1 \Delta \phi(x') dx' - \frac{8c}{\pi} \int_{-1}^1 S(x, x') \phi(x') dx' \quad (\text{IV.A.6})$$

In view of the kernel expansion (IV.4.1) and the fact that the Legendre polynomials are eigenfunctions of Δ , we easily verify that the even polynomials, $P_{2n}(x)$, are nontrivial solutions of (IV.A.5) at the respective concentrations

$$c^* = 2^{2n-2} n(2n+1) \frac{n!(n+1)!}{(2n-3)!!(2n-1)!!} \quad (\text{IV.A.7})$$

The normalized eigenfunction with the required symmetry for a nematic phase is $\sqrt{5/2} P_2(x)$, which has the simple eigenvalue

$$c^* = 6 \quad (\text{IV.A.8})$$

Eq. (IV.A.5) is a necessary though not sufficient condition for branching. Nevertheless, a formal modification [33] of section 3 of ref. 24 does show that there is a bifurcation point at this concentration and justifies the use of Taylor expansions in a small parameter μ around it

$$\psi(x) = \frac{1}{\sqrt{4\pi}} + \mu \sqrt{5/2} P_2(x) + \mathcal{O}(\mu^2) \quad (\text{IV.A.9})$$

$$c = 6 + \mu c_1 + \mathcal{O}(\mu^2) \quad (\text{IV.A.10})$$

Ref. 24 gives the following relation for c_1

$$\begin{aligned} <D_1 D_2 F\left(\frac{1}{\sqrt{4\pi}}, 6\right), (\sqrt{5/2} P_2, 1), \sqrt{5/2} P_2> c_1 \\ + \frac{1}{2!} <D_1^2 F\left(\frac{1}{\sqrt{4\pi}}, 6\right), (\sqrt{5/2} P_2, \sqrt{5/2} P_2), \sqrt{5/2} P_2> = 0 \end{aligned} \quad (\text{IV.A.11})$$

which is in fact the term linear in μ obtained by substituting the expansions in eq. (IV.A.3) and taking an inner product with $\sqrt{5/2} P_2(x)$

$$<\psi, \sqrt{5/2} P_2> \cong \int_{-1}^1 \psi(x) \sqrt{5/2} P_2(x) dx \quad (\text{IV.A.12})$$

The second Fréchet derivatives are given by

$$D_1 D_2 F\left(\frac{1}{\sqrt{4\pi}}, c^*\right), (\phi, d) = -\frac{8d}{\pi} \int_{-1}^1 S(x, x') \phi(x') dx' \quad (\text{IV.A.13})$$

and

$$\begin{aligned} D_1^2 F\left(\frac{1}{\sqrt{4\pi}}, c^*\right), (\phi, \phi) &= \sqrt{\pi} \int_{-1}^1 \phi(x') \Delta \phi(x') dx' - \sqrt{\pi} \phi(x) \int_{-1}^1 \Delta \phi(x') dx' \\ &- \frac{16c^*}{\sqrt{\pi}} \int_{-1}^1 S(x, x') \phi^2(x') dx' - \frac{32c^*}{\sqrt{\pi}} \phi(x) \int_{-1}^1 S(x, x') \phi(x') dx' \end{aligned} \quad (\text{IV.A.14})$$

Using (IV.A.11-14) we find

$$c_1 = -\frac{90}{7} \sqrt{\frac{2\pi}{5}} \quad (\text{IV.A.15})$$

In principle it is possible to determine the higher order terms in (IV.A.9 and 10) analogously.

Appendix B

We derive the Khokhlov-Semenov theorem used in section IV.8, often referring to the formalism of section VIII of the review by one of us [4] and its references. We start with the partition function of a wormlike chain (with tangential unit end vectors fixed) written as a *formal* functional integration over all possible conformations

$$Z(v_1, v_2, L) = \int_{v(0)=v_1}^{v(L)=v_2} \exp \left[-\frac{1}{2} P \int_0^L \dot{v}^2(s) ds - \int_0^L \frac{U_{scf}}{k_B T} ds + \frac{u}{P} \mathbf{e}_z \cdot \int_0^L \mathbf{v}(s) ds \right] \mathcal{D}[\mathbf{v}(s)] \quad (\text{IV.B.1})$$

where $\mathbf{v}(s)$ is the unit tangent vector of the chain at point s , the first term in the exponent is the bending energy, the second term represents the potential energy of the chain in the nematic field (which is a self-consistent field of excluded-volume type) and the third gives the potential energy as a result of the external dipolar field. The integrand of (IV.B.1) may be considered an unnormalized probability function for the conformations with fixed orientations of the end vectors $\mathbf{v}_1$ and $\mathbf{v}_2$.

Eq. (IV.B.1) *formally* corresponds to the differential equation [4,17,23]

$$\frac{\partial Z(v_1, v, s)}{\partial s} = \frac{1}{2P} \Delta_v Z(v_1, v, s) - \frac{U_{scf}}{k_B T} Z(v_1, v, s) + \frac{u}{P} \mathbf{e}_z \cdot \mathbf{v} Z(v_1, v, s) \quad (\text{IV.B.2})$$

When we now follow section (VIII.d) of ref. 4 we find for the free energy per persistence length as a result of the external field

$$\frac{\Delta F_{ext}}{k_B T} = -u \int \cos \theta f(\cos \theta) d\Omega = -u \langle P_1 \rangle \quad (\text{IV.B.3})$$

Because we can write $f(v) = f(\cos \theta)$ as [4]

$$f(v) = \frac{\int dv_1 \int dv_2 \int_0^L ds Z(v_1, v, s) Z(v, v_2, L-s)}{L \int dv_1 \int dv_2 Z(v_1, v_2, L)} \quad (\text{IV.B.4})$$

$\langle P_1 \rangle$ in eq. (IV.B.3) can be rewritten as

$$\langle P_1 \rangle = \frac{\int dv_1 \int dv_2 \int_0^L ds \int dv [(e_z \cdot v) Z(v_1, v, s) Z(v, v_2, L-s)]}{L \int dv_1 \int dv_2 Z(v_1, v_2, L)} \quad (\text{IV.B.5})$$

Substituting (IV.B.1) into eq. (IV.B.5) and combining the functional integrations with the integration over $\mathbf{v}$ give

$$\langle P_1 \rangle = \frac{\int \{ L^{-1} \int_0^L \mathbf{e}_z \cdot \mathbf{v}(s) ds \} \exp \left[-\frac{1}{2} P \int_0^L \dot{\mathbf{v}}^2(s) ds - \int_0^L \frac{U_{scf}}{k_B T} ds + \frac{u}{P} \mathbf{e}_z \cdot \int_0^L \mathbf{v}(s) ds \right] \mathcal{D}[\mathbf{v}(s)]}{\int d\mathbf{v}_1 \int d\mathbf{v}_2 Z(\mathbf{v}_1, \mathbf{v}_2, L)} \quad (\text{IV.B.6})$$

where the functional integration now takes place without restrictions. The susceptibility χ_0 is readily derived from this expression for $\langle P_1 \rangle$

$$\chi_0 = \left. \frac{\partial \langle P_1 \rangle}{\partial u} \right|_{u=0} = \frac{1}{LP} \frac{\int \{ \int_0^L \mathbf{e}_z \cdot \mathbf{v}(s) ds \}^2 \exp \left[-\frac{1}{2} P \int_0^L \dot{\mathbf{v}}^2(s) ds - \int_0^L \frac{U_{scf}}{k_B T} ds \right] \mathcal{D}[\mathbf{v}(s)]}{\int d\mathbf{v}_1 \int d\mathbf{v}_2 Z(\mathbf{v}_1, \mathbf{v}_2, L)} \quad (\text{IV.B.7})$$

which shows that

$$\chi_0 = \frac{1}{LP} \langle R_z^2 \rangle_0 \quad (\text{IV.B.8})$$

as we set out to prove.

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- [25] The upper limit in eq. (IV.8.14) is taken somewhat lower than 1 in order to avoid a divergence due to $(1 - x^2)^{-1}$ which was previously compensated by $\left[\int_y^1 xf(x)dx\right]^2$. Note that the integration region near $x = 1$ in eq. (IV.8.14) is subdominant.
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- [27] T.Odijk, Liq.Cryst. 1, 553 (1986).
- [28] That is the very reason why it was chosen in the first place.
- [29] T.Odijk, J.Phys.Chem. 91, 6060 (1987).
- [30] T.Odijk, Macromolecules 20, 1423 (1987).
- [31] Eq. (IV.8.19) is a numerical relation between the susceptibility and the Gaussian parameter α . Thus, it is merely illustrative and convenient but not asymptotic.
- [32] Thus, there are about L/g steps of average length g . The fluctuation in the step length is of order g and the distribution is Gaussian.
- [33] Our terminology is deliberately vague since our reasoning lacks any rigor. For a complete proof one must choose a Banach space like L_2 (or perhaps L_4) but the usual theorems do not apply since Δ is an unbounded operator. Rearrangement of eq. (IV.A.3) with the help of a suitable Green function does lead to an equation involving only compact and bounded operators. But we have been unable to proof the compactness of the total operator which is needed to apply standard theorems [24].

CHAPTER V

THE ISOTROPIC-NEMATIC PHASE TRANSITION AND OTHER PROPERTIES OF A SOLUTION OF SEMIFLEXIBLE POLYELECTROLYTES

submitted for publication

V.0 Abstract

We extend previous work (G.J. Vroege and T. Odijk, chapter IV) on the formation of nematic liquid crystals from uncharged semiflexible polymers to the charged case. The polyelectrolytes are modelled as long slender wormlike cylinders interacting via both hard-core and electrostatic repulsions in the second virial approximation. Analogously to rodlike polyelectrolytes it is possible to describe the result of charge by introducing an effective diameter and a twisting effect. We then calculate numerically the orientational distribution function as a function of concentration. We determine the effect of charge on the phase transition and -in the nematic phase- its influence on the order parameter and the global persistence length (directly connected to the splay elastic modulus). Although the phase transition concentrations are clearly dependent of charge, the properties of the nematic phase at the transition are not - in contrast to the result for rodlike polyelectrolytes.

V.1 Introduction

It is well known that a solution of stiff, anisometric particles can form a nematic liquid crystal above a certain concentration. Such a lyotropic liquid crystal may consist of viruses (like the long known example of Tobacco Mosaic Virus [1]), biological macromolecules (like DNA [2] or the polysaccharide xanthan [3]), synthetic macromolecules (like polyaramides [4]) or even micelles [5]. For these very stiff molecules liquid crystal formation already takes place at very low volume fractions. The basis of one of the ways to view lyotropic liquid crystals was laid by Onsager [6], who described the interaction between the particles -analogously to a gas- by a virial series in the concentration, retaining only the second virial term for the low volume fractions involved. In an orientationally anisotropic system like a nematic liquid crystal the free energy also contains an orientational entropy term taken by Onsager as that for perfect hard rods. However, over thirty years later Khokhlov and Semenov [7] recognized that most macromolecules cannot be considered as perfectly rigid and derived an expression for the orientational entropy of semiflexible macromolecules modelled as wormlike chains. This flexibility introduces more possibilities for the configurations of the macromolecule which comprise undulations around the director (on an average length scale introduced as the deflection length [8]) and hairpins (connected to the so-called global persistence length [9,10]).

Another important extension is the effect of charge, which plays a role in most of the examples mentioned above. Onsager [6] already introduced a larger effective diameter to account for that and later a careful analysis for charged

rods was given by Stroobants et al. [11] revealing a second effect caused by the tendency of the rods to twist away from the parallel configuration. We propose to combine these notions with the wormlike chain model to describe semiflexible polyelectrolytes on the basis of a numerical analysis given in a previous article [10] (chapter IV of this thesis). In this context it is also useful to note the review by Odijk [12] which discusses all theories mentioned. Finally, ref. 22 gives a qualitative discussion of the elastic moduli of a liquid-crystalline solution of semiflexible polyelectrolytes.

In the following we sketch the theoretical framework needed in section V.2 and the numerical analysis and results in section V.3 and V.4 respectively. An analytical perturbation method is given in section V.5 and section V.6 discusses the global persistence length and splay elastic constant. Finally, section V.7 presents a numerical example on xanthan and some concluding remarks.

V.2 Formalism

Here we consider a volume V of a solution of N_L very long, semiflexible polyelectrolytes (i.e. length $L \gg$ persistence length $P \gg$ diameter D) and an excess of 1-1 electrolyte, the total being in dialytic equilibrium with a pure salt solution. The condition $L \gg P$ is important because it implies that the majority of the points on the chain is far from the chain ends so that we can use a single orientational distribution function, $f(\cos\theta)$, independent of the position on the chain (θ is the angle between the tangential vector of the chain at a certain point and the director; in the uniaxial nematic phase f only depends on θ and not on the azimuthal angle ϕ).

The second condition $P \gg D$ justifies a second virial approximation of the free energy because of the low volume fractions involved:

$$\frac{\Delta F}{Vk_B T} = \text{cst} - \frac{\Delta S_{\text{or}}}{V} + B_2(N_L/V)^2 + \mathcal{O}(N_L/V)^3 \quad (\text{V.2.1})$$

with B_2 the second virial coefficient. The orientational entropy ΔS_{or} is associated [7] with all possible configurations which chains of persistence length P can describe when the total chain length in solution is $N_L L$

$$\Delta S_{\text{or}} = \frac{N_L L}{P} \pi \int_{-1}^1 f^{1/2}(\cos\theta) \Delta f^{1/2}(\cos\theta) d\cos\theta \equiv -\frac{N_L L}{P} \sigma_P(f) \quad (\text{V.2.2})$$

where the operator $\Delta \equiv \frac{\partial}{\partial \cos\theta} (1 - \cos^2\theta) \frac{\partial}{\partial \cos\theta}$ is the orientational part of the Laplacian for uniaxial symmetry.

For the two-particle interaction we first consider a solution of N_l charged rods of length l and diameter D , with N_l such that $N_l l = N_L L$. According to ref. 11 the second virial coefficient $B_2(l)$ can be determined from the hard-core repulsion and an electrostatic potential of mean force

$$\frac{w^e l}{k_B T} = \frac{A' e^{-\kappa(x-D)}}{\sin \gamma} \quad (\text{V.2.3})$$

between two rods making an angle γ and having a nearest distance between their centerlines of x . κ^{-1} is the Debye screening length, the dimensionless parameter A' depends on the polyelectrolyte properties and is extensively discussed in ref. 11. In the following A' must be ≥ 2 . The result is

$$B_2(l) = \frac{\pi l^2 \tilde{D}}{4} [\rho(f) + h\eta(f)] \quad (\text{V.2.4})$$

with the usual hard-core part [6]

$$\begin{aligned} \rho(f) &= \frac{4}{\pi} \langle \langle \sin \gamma \rangle \rangle \\ &\equiv \frac{4}{\pi} \iiint \sin \gamma f(\cos \theta) f(\cos \theta') d\cos \theta d\phi d\cos \theta' d\phi' \end{aligned} \quad (\text{V.2.5})$$

and the effect of electrostatic repulsion reflected both in a larger effective diameter

$$\tilde{D} = D \left[1 + \frac{\ln A' + C_E + \ln 2 - 1/2}{\kappa D} \right] \quad (\text{V.2.6})$$

($C_E = 0.5772\dots$ is Euler's constant) and in a twisting effect originating from the $\sin \gamma$ -dependence of $w^e l$

$$\eta(f) = \frac{4}{\pi} \langle \langle -\sin \gamma \ln(\sin \gamma) \rangle \rangle - (\ln 2 - 1/2) \rho(f) \quad (\text{V.2.7})$$

linear in the twisting parameter

$$h = \frac{1}{\kappa \tilde{D}} \quad (\text{V.2.8})$$

In the free energy $B_2(l)$ always appears in combination with N_l^2 (cf. eq. (V.2.1)), which means that the two-particle interaction scales like $l^2 N_l^2$. As a consequence it does not change when we combine the rods forming longer rods while keeping the total chain length $N_l l$ constant. However, it is equally possible to combine the rods to wormlike chains with a persistence length $P \gg l$ in which case the interaction free energy will also be $B_2(l)(N_l/V)^2 = B_2(L)(N_L/V)^2$ (or analogously $B_2(P)(N_P/V)^2$) to zeroth order. This reflects the fact that the two-particle interaction occurs on a local scale where the wormlike

polymers can be treated as rods. This leads to a total free energy per persistence length segment

$$\frac{\Delta F_P}{k_B T} = \frac{\Delta F}{N_P k_B T} = \text{cst} + \sigma_P(f) + c[\rho(f) + h\eta(f)] \quad (\text{V.2.9})$$

where a scaled concentration

$$c \equiv \frac{\pi}{4} P^2 \tilde{D}(N_P/V) = \frac{\pi}{4} PL \tilde{D}(N_L/V) \quad (\text{V.2.10})$$

has been introduced.

Finally it is important to point out that in the case of polyelectrolytes the total persistence length P has an intrinsic part P_{int} (the persistence length of the corresponding uncharged polymer) and an electrostatic part P_{el}

$$P = P_{\text{int}} + P_{\text{el}} \quad (\text{V.2.11})$$

P_{el} was first determined by Odijk [13,14] and independently by Skolnick and Fixman [15] in the Debye-Hückel approximation

$$P_{\text{el}} = \frac{f^2 Q}{4 A_c^2 \kappa^2} \quad (\text{V.2.12})$$

where $Q \equiv \frac{e^2}{\epsilon k_B T}$ (e : elementary charge, ϵ : dielectric permittivity) is the Bjerrum length, A_c is the contour distance between two neighboring charges on the polyelectrolyte chain and f derives from the Oosawa-Manning [16,17] counterion condensation picture

$$\begin{aligned} f &= 1 && \text{for } A_c/Q > 1 \\ f &= A_c/Q && \text{for } A_c/Q < 1 \end{aligned} \quad (\text{V.2.13})$$

Later Le Bret [18,19] and Fixman [20] extended the result using the nonlinear Poisson-Boltzmann equation and found that eq. (V.2.12) is a good approximation for electrolyte concentrations less than about 0.01 M (depending on the detailed polyelectrolyte properties). Above this concentration the approximation gets worse but it does not influence the results of this article very much because in that case the relation $P_{\text{int}} \gg P_{\text{el}}$ must apply anyway in order to fulfil $P \gg \tilde{D}$ (which replaces the condition $P \gg D$ in the polyelectrolyte case).

V.3 Numerical Analysis

For a certain concentration c the distribution function $f(\cos\theta)$ is found by minimizing the free energy (V.2.9) which leads to a nonlinear integrodifferential equation as in chapter IV

$$-\frac{1}{2}\Delta\psi(x) = \left[E - 16c \int_{-1}^1 S(x,x') \psi^2(x') dx' \right] \psi(x) \quad (V.3.1)$$

with $x \equiv \cos\theta$, $\Delta \equiv \frac{\partial}{\partial x}(1-x^2)\frac{\partial}{\partial x}$ and $\psi(x) \equiv f^{1/2}(x)$. E is a Lagrange multiplier originating from the normalization condition

$$2\pi \int_{-1}^1 f(x) dx = 2\pi \int_{-1}^1 \psi^2(x) dx = 1 \quad (V.3.2)$$

The kernel $S(x,x')$ is now a sum

$$S(x,x') = S_0(x,x') + hS_1(x,x') \quad (V.3.3)$$

of two parts both of which can be written as a bilinear expansion in Legendre polynomials

$$S_0(x,x') \equiv \frac{1}{2\pi} \int_0^{2\pi} \sin\gamma(x,x',\phi-\phi') d(\phi-\phi') \quad (V.3.4a)$$

$$= \sum_{n=0}^{\infty} d_{2n} P_{2n}(x) P_{2n}(x') \quad (V.3.4b)$$

and

$$S_1(x,x') \equiv \frac{1}{2\pi} \int_0^{2\pi} \sin\gamma[-\ln(\sin\gamma) - \ln 2 + 1/2] d(\phi-\phi') \quad (V.3.5a)$$

$$= \sum_{n=0}^{\infty} d'_{2n} P_{2n}(x) P_{2n}(x') \quad (V.3.5b)$$

Here [21,10] $d_0 = \pi/4$, $d_2 = -5\pi/32$,

$$d_{2n} = - \frac{\pi(4n+1)(2n-3)!!(2n-1)!!}{2^{2n+2}n!(n+1)!} \quad (n \geq 2) \quad (V.3.6)$$

and [22] $d'_0 = 0$,

$$d'_{2n} = d_{2n} \left[\sum_{k=0}^{n-1} \frac{1}{2(k+2)} + \frac{1}{2k-1} \right] \quad (n \geq 1) \quad (V.3.7)$$

Now it is convenient to expand $\psi(x)$ in Legendre polynomials

$$\psi(x) = \frac{1}{\sqrt{4\pi}} \sum_{n=0}^{\infty} a_{2n} P_{2n}(x) \quad (V.3.8)$$

because these polynomials are eigenfunctions of Δ

$$\Delta P_{2n}(x) = -2n(2n+1) P_{2n}(x) \quad (V.3.9)$$

Furthermore, with expansions (V.3.4b, 5b and 8) the integral in eq. (V.3.1) gives rise to the following integrals

$$I_{k,l,m} \equiv \frac{1}{2} \int_{-1}^1 P_k(x) P_l(x) P_m(x) dx \quad (V.3.10a)$$

$$= \frac{(k+l-m)!(k-l+m)!(-k+l+m)!}{(k+l+m+1)!} \left[\frac{\left(\frac{k+l+m}{2}\right)!}{\left(\frac{k+l-m}{2}\right)!\left(\frac{k-l+m}{2}\right)!\left(\frac{-k+l+m}{2}\right)!} \right]^2 \quad (V.3.10b)$$

for $(k+l+m)$ even and $(k+l-m)$, $(k-l+m)$ and $(-k+l+m)$ not negative, otherwise $I_{k,l,m} = 0$. With these expansions the nonlinear integrodifferential equation (V.3.1) can be reduced to an infinite set of nonlinear algebraic equations in the unknown variables a_{2n}

$$\frac{j(2j+1)}{(4j+1)} a_{2j} = \frac{E}{(4j+1)} a_{2j} - \frac{8c}{\pi} \sum_{k,l,m,n=0}^{\infty} (d_{2k} + h d_{2k}') a_{2l} a_{2m} a_{2n} I_{2k,2l,2m} I_{2k,2n,2j} \quad (V.3.11)$$

in combination with one extra relation derived from the normalization condition (V.3.2)

$$\sum_{n=0}^{\infty} \frac{a_{2n}^2}{(4n+1)} = 1 \quad (V.3.12)$$

These equations can be solved numerically for fixed concentration c or they can be combined with the coexistence relations to determine the phase transition from an isotropic solution (of concentration c_i) to a nematic solution (of concentration c_a) [12]

$$c_i^2 = c_a^2(\rho + h\eta) \quad (V.3.13)$$

$$2c_i = \sigma_P + 2c_a(\rho + h\eta) \quad (V.3.14)$$

where η can be written as

$$\eta(f) = \frac{4}{\pi} \sum_{k=0}^{\infty} d_{2k}' \left[\sum_{l,m=0}^{\infty} a_{2l} a_{2m} I_{2k,2l,2m} \right]^2 \quad (V.3.15)$$

The analogous expressions for σ_p and ρ are given by eqs. (IV.6.2 & 3). The numerical method of solution is the same as in chapter IV, to which we refer for details. The results are given in the next section.

V.4 Numerical Results

For low concentrations eq. (V.3.1) only has an isotropic solution

$$\psi(x) = \frac{1}{\sqrt{4\pi}} \quad (\text{V.4.1})$$

Increasing c , we reach a bifurcation point c^* where an anisotropic solution branches off from the isotropic one. We determined this point similarly to chapter IV and found $c^* = 6(1-\frac{3}{4}h)^{-1}$ (note that the same h -dependent factor appears in the bifurcation point for charged rods [12]). Moreover, we determined the behavior of the anisotropic branch near the bifurcation point. Taking

$$c = \frac{1}{1-\frac{3}{4}h} [6 + \nu] \quad (\text{V.4.2})$$

where ν is small, we find for the square root of the distribution function

$$\psi(x) = \frac{1}{\sqrt{4\pi}} [1 - \frac{7}{18}\nu P_2(x) + \mathcal{O}(\nu^2)] \quad (\text{V.4.3})$$

Note that the coefficient of $P_2(x)$ is independent of h , which indicates that to linear order in ν the deviation from the isotropic solution is the same for all h provided we scale the concentration by a factor of $(1-\frac{3}{4}h)$. This is illustrated in fig.1 where a measure of the anisotropic part of $\psi(x)$, viz. $\sqrt{1-a_0^2}$, is plotted against this scaled concentration

$$c^\dagger \equiv c(1-\frac{3}{4}h) \quad (\text{V.4.4})$$

(the branches with order parameter $S < 0$ are a natural extension of those with $S > 0$ but they do not have physical significance, as explained in chapter IV, so we will not consider them any further). To higher order in ν differences do appear for possible values of h because of the nonlinear character of the integrodifferential equation (V.3.1). In tables 1 and 2 we give numerical results for the order parameter S and the difference in free energy between an isotropic and an anisotropic solution of the same concentration $c^\dagger$. As can be seen, for the same scaled concentration $c^\dagger$ the solution is more anisotropic and more favorable in free energy the greater h is (and of course the greater $c^\dagger$ is).

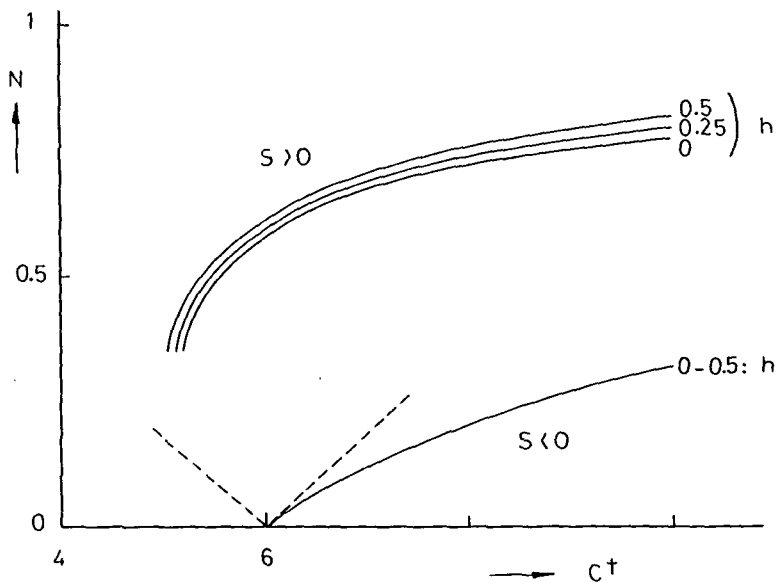


Fig. 1 A measure of the anisotropy of the distribution function $N \equiv \sqrt{1-a_0^2}$ as a function of scaled concentration $c^\dagger$. The $N = 0$ axis denotes the isotropic solution. The upper three solid lines give the anisotropic solutions with $S > 0$ for values of $h = 0, 0.25$ and 0.5 . The lower solid line is the $S < 0$ solution for all three values of h . Dashed lines give the linearized solutions near the bifurcation point (derived from eq(V.4.3)).

$c^\dagger$	$S(h=0)$	$S(h=0.1)$	$S(h=0.25)$	$S(h=0.5)$
6	0.5448	0.5494	0.5584	0.5820
8	0.6785	0.6830	0.6914	0.7130
10	0.7358	0.7404	0.7489	0.7703
12	0.7711	0.7758	0.7844	0.8057
15	0.8062	0.8109	0.8196	0.8403
20	0.8424	0.8472	0.8557	0.8751
25	0.8654	0.8700	0.8782	0.8964
35	0.8935	0.8979	0.9055	0.9215

Table 1 Order parameter S for different values of charge parameter h as a function of scaled concentration $c^\dagger$.

$c^\dagger$	$\Delta F_{P,i} - \Delta F_{P,a}$			
	(h=0)	(h=0.1)	(h=0.25)	(h=0.5)
6	0.108	0.110	0.118	0.136
8	0.614	0.627	0.653	0.728
10	1.277	1.305	1.359	1.511
12	2.038	2.083	2.171	2.422
15	3.309	3.384	3.536	3.966
20	5.667	5.810	6.091	6.892
25	8.244	8.465	8.902	10.14
35	13.84	14.25	15.05	17.33

Table 2 Difference in (scaled) free energy (V.2.9) between the isotropic and the anisotropic state as a function of $c^\dagger$ for different values of h .

Numerical results for the isotropic-nematic phase transition are given in table 3 for different values of the twisting parameter h . What strikes us most is the fact that the scaled transition concentrations c_i and c_a (this time scaled only by $\frac{\pi}{4}PL\tilde{D}$ -see eq. (V.2.10)- and not by $(1-\frac{3}{4}h)$) clearly change with h but that the properties of the anisotropic phase at the phase transition remain nearly constant (only at physically unrealistic values above $h=0.5$ do the properties change significantly). This indicates that the distribution function at the phase transition in practice hardly depends upon h . This is in marked contrast with the results for charged rods where the distribution function at the phase transition clearly depends strongly on h [11].

h	c_i	c_a	S	σ_P	ρ	η	χ_0
0	5.124	5.509	0.4617	0.7176	0.8648	0.0991	6.506
0.1	5.544	5.924	0.4595	0.7106	0.8661	0.0981	6.400
0.2	6.036	6.412	0.4583	0.7068	0.8668	0.0976	6.334
0.3	6.621	6.995	0.4583	0.7073	0.8667	0.0976	6.316
0.4	7.327	7.701	0.4601	0.7133	0.8657	0.0984	6.359
0.5	8.194	8.575	0.4642	0.7272	0.8632	0.1001	6.491
0.6	9.286	9.679	0.4718	0.7533	0.8585	0.1033	6.761
0.8	12.596	13.055	0.5075	0.8860	0.8355	0.1193	8.322
1.0	19.068	19.823	0.6212	1.4514	0.7489	0.1765	18.32

Table 3 Phase transition concentrations c_i and c_a , order parameter S , entropy σ_P (V.2.2), interaction terms ρ and η (V.2.5&7) and susceptibility χ_0 (V.6.2) as a function of charge parameter h .

The above mentioned numerical results can be checked in several ways.

Firstly, the analytically determined behavior near the bifurcation point (eqs. (V.4.2) and (V.4.3)) can be verified to be consistent with the numerical solution. Secondly, we can formulate a perturbation expansion for low values of h which we will consider in the next paragraph. Finally, also for low values of h , a relation between σ_p and ρ can be derived, which is treated in the appendix.

V.5 Analytical Theory for Small h

The method used here is due to Odijk [11,12]. For reasons of clarity we will briefly sketch the lines of reasoning. We start with the Onsager trial function for representing the distribution function

$$f(x) = \frac{\alpha \cosh(\alpha x)}{4\pi \sinh(\alpha)} \quad (V.5.1)$$

with one adjustable parameter α . With the use of that, asymptotic expressions (valid for large α) can be derived for σ_p (specific for semiflexible chains [12]), ρ and η (both equal to the expressions for rods [11])

$$\sigma_p(\alpha) \sim \frac{1}{4}(\alpha - 1) + \mathcal{O}(\exp(-\alpha)) \quad (V.5.2)$$

$$\rho(\alpha) \sim \frac{4}{\sqrt{\pi\alpha}} \left[1 - \frac{15}{16\alpha} + \frac{105}{512\alpha^2} + \frac{315}{8192\alpha^3} + \dots \right] \quad (V.5.3)$$

$$\eta(\alpha) \sim \frac{2}{\sqrt{\pi\alpha}} \left\{ (1\alpha - 2\ln 2 - 1 + C_E) \left[1 - \frac{15}{16\alpha} + \frac{105}{512\alpha^2} + \frac{315}{8192\alpha^3} + \dots \right] + \left[\frac{5}{2\alpha} - \frac{67}{32\alpha^2} - \frac{307}{1024\alpha^3} + \dots \right] \right\} \quad (V.5.4)$$

Minimizing the free energy (V.2.9) gives

$$\sigma_p'(\alpha) + c_a[\rho'(\alpha) + h\eta'(\alpha)] = 0 \quad (V.5.5)$$

For $h=0$ this can be solved in combination with the coexistence equations (V.3.13 and 14) giving [12]

$$\alpha_0 = 6.502 \quad c_{i,0} = 5.409 \quad c_{a,0} = 6.197 \quad (V.5.6)$$

the index 0 denoting the zeroth order solution. As discussed in chapter IV this deviates about 10-15 % from the exact numerical results. Because of the $\ln\alpha$ dependence of $\eta(\alpha)$ it is not possible to find a closed expression for c_i and c_a

in terms of h , but we can develop a perturbation theory by writing

$$c_i = c_{i,0} + \delta c_i \quad (\text{V.5.7a})$$

$$c_a = c_{a,0} + \delta c_a \quad (\text{V.5.7b})$$

$$\alpha = \alpha_0 + \delta \alpha \quad (\text{V.5.7c})$$

where the δ -type terms are assumed to be linear in h for small h . For functions depending on α we can make a Taylor expansion around α_0

$$g(\alpha) = g(\alpha_0) + g'(\alpha_0)\delta\alpha + \mathcal{O}(h^2) \quad (\text{V.5.8})$$

This can be used in eqs. (V.5.5) and (V.3.13 and 14) retaining only terms linear in h . This results in a set of 3 linear equations in δc_i , δc_a and $\delta \alpha$

$$\rho'(\alpha_0)\delta c_a + [\sigma_P''(\alpha_0) + c_{a,0}\rho''(\alpha_0)]\delta\alpha = -c_{a,0}\eta'(\alpha_0)h \quad (\text{V.5.9a})$$

$$2c_{i,0}\delta c_i - 2c_{a,0}\rho(\alpha_0)\delta c_a - c_{a,0}^2\rho'(\alpha_0)\delta\alpha = c_{a,0}^2\eta(\alpha_0)h \quad (\text{V.5.9b})$$

$$2\delta c_i - 2\rho(\alpha_0)\delta c_a - [\sigma_P'(\alpha_0) + 2c_{a,0}\rho'(\alpha_0)]\delta\alpha = 2c_{a,0}\eta(\alpha_0)h \quad (\text{V.5.9c})$$

Using asymptotic expressions (V.5.2-4) and zeroth order values (V.5.6) this can be easily solved, yielding [23]

$$\delta c_i = 4.19h \quad (\text{V.5.10a})$$

$$\delta c_a = 4.10h \quad (\text{V.5.10b})$$

$$\delta \alpha = -0.018h \quad (\text{V.5.10c})$$

These values for the change in transition concentrations are only 7% higher than the numerical values (for small h) $\delta c_i = 3.90h$ and $\delta c_a = 3.83h$, which is of the same magnitude as the error in the zeroth order solution. The very small negative change of α also agrees with the conclusion from the numerical results that the distribution function at the phase transition does hardly depend on h .

V.6 The Global Persistence Length and the Splay Modulus

The persistence length P of equation (V.2.11) can be considered as a local property of the wormlike chain: its intrinsic part represents the local chemical structure of the chain and its electrostatic part originates from local electrostatic interactions. This property is thus found in the mean square of the endpoint distance for an isolated chain: $\langle R^2 \rangle = 2LP$. In the nematic phase a semiflexible chain is not isolated but it will have interactions with neighboring molecules, as a consequence of which it will stretch itself along the director.

However, for entropic reasons it is favorable to fold back now and again forming hairpins. The configuration which a single chain then describes can be viewed as a random walk in one dimension with a mean square end-to-end distance (along the director) given by

$$\langle R_z^2 \rangle = 2Lg \quad (\text{V.6.1})$$

which defines the global persistence length g as a measure of the mean distance between consecutive hairpins. In chapter IV we derived an exact expression for the relation between the global and local persistence lengths g and P

$$\chi_0 \equiv \frac{2g}{P} = 4\pi \int_0^1 \frac{1}{(1-y^2)\psi^2(y)} \left[\int_y^1 2x\psi^2(x) dx \right]^2 dy \quad (\text{V.6.2})$$

which is also valid here because the two-particle interaction term still only depends on $\sin\gamma$ (in terms of chapter IV we have $\rho_K(f) = \rho(f) + h\eta(f)$ in eq. (IV.9.1)). Thus after having obtained $\psi(x)$ numerically in section V.4 we can apply eq. (V.6.2) to determine the global persistence length.

In table 4 we give χ_0 for a number of h 's as a function of the scaled concentration $c^\dagger$. As can be seen, the numerical values only depend slightly on h but very much on $c^\dagger$. The values of χ_0 for different h 's at the phase transition (table 3) reflect the fact that the distribution function hardly changes for realistic h -values.

$c^\dagger$	$\chi_0(h=0)$	$\chi_0(h=0.1)$	$\chi_0(h=0.25)$	$\chi_0(h=0.5)$
6	11.99	12.41	13.26	15.92
7	29.51	30.89	33.69	42.83
8	62.28	66.11	73.78	100.0
9	123.3	132.1	151.1	219.0
10	233.3	253.2	296.9	460.8
12	767.0	854.6	1054	1880
15	3948	4578	6099	1.337 10^4
18	1.791 10^4	2.160 10^4	3.104 10^4	8.316 10^4
20	4.642 10^4	5.746 10^4	8.680 10^4	2.648 10^5
25	4.299 10^5	5.679 10^5	9.679 10^5	4.036 10^6
35	2.28 10^7	3.39 10^7	7.25 10^7	5.48 10^8

Table 4 Susceptibility χ_0 (V.6.2) for different values of charge parameter h as a function of scaled concentration $c^\dagger$

In chapter IV we also indicated that the occurrence of hairpins can influence the splay elastic modulus because in a splayed nematic the hairpins are not distributed homogeneously in space

$$K_1 = (2/\pi^3)^{1/2} (g/P) c(k_B T/\tilde{D}) \quad (L \gg g) \quad (V.6.3)$$

When the length of the molecules gets shorter than the global persistence length we can use the arguments originally developed for rods by Meyer [24] obtaining

$$K_1 = \pi^{-1} (L/P) c(k_B T/\tilde{D}) \quad (L < g) \quad (V.6.4)$$

As a function of concentration K_1 will first grow very fast according to eq. (V.6.3) (because of the very fast increase of g as a function of concentration) until all hairpins have disappeared (when $L \simeq g$) and the behavior of K_1 changes to that of eq. (V.6.4).

V.7 Discussion

One of the main conclusions of this chapter is the fact that the distribution function at the phase transition is virtually the same for all physically attainable values of the twisting parameter h (i.e. the distribution function is independent of the diameter and the linear charge density of the polyelectrolyte as well as the ionic strength). This implies that properties like the order parameter S and the ratio between the global and local persistence lengths (g/P) are independent of h as well. One could wonder if there is a special reason why this behavior for long semiflexible polyelectrolytes is so different from that of rigid rodlike polyelectrolytes, where e.g. the order parameter depends strongly on h . A seemingly plausible explanation is that two semiflexible chains can locally cross at rather large angles (which is favorable as to electrostatic energy) but remain more or less parallel on a global scale, while perfect rods clearly do not have this opportunity. However, this assertion cannot be right because we assumed a locally rodlike interaction for semiflexible chains and one single distribution function for all chain segments, so that the obtained constancy with h must be determined by the specific numerical values involved.

In contrast with the distribution function at the phase transition, the transition concentrations themselves certainly vary with h . For practical use we present a heuristic formula for these concentrations which can be derived from the coexistence equations (V.3.13 & 14) by taking σ_p , ρ and η constant at their values for $h=0$ (see table 3). Then c_i and c_a can easily be solved

$$c_i = \frac{0.3588}{1-\sqrt{X}} \quad (\text{V.7.1a})$$

$$c_a = \frac{0.3588}{\sqrt{X}-X} \quad (\text{V.7.1b})$$

where $X = 0.8648 + 0.0991h$. These give excellent agreement with the numerical values in table 3, the relative error slowly increasing to 0.06% at $h=0.5$. Surprisingly, at $h=1$ the error is still only 3% although σ_p now differs by a factor of 2 from that at $h=0$ so the conditions under which the formulas were derived certainly are not fulfilled anymore. Moreover, for $h=1.364$ a singularity appears in eq. (V.7.1), whereas we would expect this at $h=1.333...$ from eq. (V.4.2).

At this point it might be useful to illustrate the results of this article by taking an example based on the parameters of the polysaccharide xanthan, tabulating the intermediate results of the calculations in table 5. It seems established now [25-27] that one of the forms (depending on the preparation) of the polyelectrolyte xanthan is a double helix with an intrinsic persistence length P_{int} of $1.06 \cdot 10^3 \text{ \AA}$, a diameter D of $22 \text{ \AA}$ and -for the specific sample of ref. 26 where the degree of pyruvation of the side chains was 0.4- a mean contour distance between consecutive charges A_c of $3.33 \text{ \AA}$. We will concentrate on the highest molecular weight described in ref. 26, viz. $3.94 \cdot 10^6$, which corresponds to a contour length L of $2.03 \cdot 10^4 \text{ \AA}$ and implies an L/P ratio of about 19, high enough to apply our theory. When dissolved in an aqueous NaCl solution this polyelectrolyte is known to give a transition to a cholesteric phase as a function of its concentration [3]. We suppose that this phase transition will be very similar to the isotropic-nematic transition described in this article so that we can use the above theory. To determine the effective diameter $\tilde{D}$ of the macromolecule as a function of the NaCl concentration we first need to know A' appearing in eq. (V.2.6). As sketched in ref. 11 and chapter II this constant can be derived from the fact that the (scaled) electrical potential around a single rodlike macroion always has a far-field form of

$$\frac{e\psi^{\text{el}}}{k_B T} \sim \Gamma K_0(\kappa r) \quad (\text{V.7.2})$$

with r the distance from the centerline. The proportionality constant Γ appears in the expression for A'

$$A' = \frac{1}{2} \pi \Gamma^2 (Q\kappa)^{-1} e^{-\kappa D} \quad (\text{V.7.3})$$

with the Bjerrum length $Q \approx 7.135 \text{ \AA}$ in water of 25°C . For different NaCl concentrations we determined Γ from ref. 28 and the corresponding A' from the above equation, which values were substituted in eqs. (V.2.6 and 8) to obtain $\tilde{D}$ and the twisting parameter h . The electric part of the persistence length (eq. (V.2.12) with $f = A_c/Q$) for each NaCl concentration must be combined with the

intrinsic value of $1.06 \cdot 10^3 \text{ \AA}$ to obtain the total value P . Now we find the scaled phase transition concentrations from eqs. (V.7.1a and 1b), the real number densities by dividing by $(\pi/4)PL\tilde{D}$ (see eq. (V.2.10)) and the real concentrations ρ_i and ρ_a by multiplying by the molecular weight of $3.94 \cdot 10^6$. From the values for h and P we derive a global persistence length of $3.4 \cdot 10^3 \text{ \AA}$ (see table 3 and definition (V.6.2)) for all salt concentrations considered. This is about 6 times shorter than the total contour length, which means that the effect of hairpins should show up in the splay elastic modulus (see section V.6). Finally, we point out that we neglected the contribution to the ionic strength of the Na^+ counterions of the xanthan itself given by (N_L/V) times the number of charges per macromolecule, L/A_c . Especially for $[\text{NaCl}] = 0.03 \text{ M}$ this is not completely justified because the counterions give a contribution of about one third of the total ionic strength.

[NaCl]	(mol/l)	1	0.3	0.1	0.03
κ^{-1}	$\text{\AA}$	3.04	5.55	9.61	17.55
Γ	-	61.0	13.5	6.39	3.93
A'	-	1.80	4.24	8.74	17.1
$\tilde{D}$	$\text{\AA}$	26.1	34.3	50.2	85.3
h	-	0.116	0.162	0.191	0.206
P_{el}	$\text{\AA}$	0.324	1.08	3.24	10.8
P	$10^3 \text{\AA}$	1.06	1.06	1.06	1.07
c_i	-	5.62	5.84	5.99	6.07
c_a	-	6.00	6.22	6.37	6.45
$(N_L/V)_i$	10^{-5}M	2.12	1.67	1.17	0.693
$(N_L/V)_a$	10^{-5}M	2.26	1.78	1.25	0.736
ρ_i	g/l	83.5	65.8	46.1	27.3
ρ_a	g/l	89.0	70.1	49.3	29.0

Table 5 Intermediate results in the calculations for xanthan (see text).

As we see from table 5, at the given NaCl concentrations the electrostatic persistence length gives virtually no contribution to the total persistence length whereas the effective diameter changes markedly with the ion concentration. This has the implication that below a NaCl concentration of 0.1 M the ratio $P/\tilde{D}$ is less than 20 where higher virial coefficients come into play. Eventually, for very low ion concentrations $\tilde{D}$ increases like κ^{-1} while P_{el} grows faster as κ^{-2} so that the second virial approximation could improve again (but this might even be the case for flexible polyelectrolytes, see ref. 12). This means that only for extremely stiff polyelectrolytes can our theory be valid over the whole range of ionic strength. However, then it will probably be impossible to fulfil the other condition $L \gg P$ under which our theory was derived. This stresses once more the need to obtain reliable numerical results for arbitrary contour length. To our knowledge, there are no experiments available at this moment to test our theory but -as sketched above- they are certainly feasible for reasonably high ionic strengths.

Acknowledgement

The author thanks Prof.Dr. Theo Odijk for helpful discussions.

Appendix

In this appendix we first derive an expression for δc_i (see (V.5.7a)) in terms of properties of uncharged polymers. From eq. (V.5.5) for $h=0$ at the phase transition we derive

$$\sigma_P'(\alpha_0) + c_{a,0}\rho'(\alpha_0) = 0 \quad (V.A.1)$$

This relation can be used to eliminate $\sigma_P'(\alpha_0)$ from eq. (V.5.9c) whereupon δc_i can be found by combination of the obtained equation with eq. (V.5.9b)

$$\delta c_i = \frac{c_{a,0}^2 \eta(\alpha_0)}{2(c_{a,0} - c_{i,0})} h \quad (V.A.2)$$

When we substitute the respective numerical values of the zeroth order quantities we obtain eq.(V.5.10a).

We can also obtain a more formal relationship between σ_P and ρ for small

h by writing $\psi(x)$ to linear order in h as

$$\psi(x) = \psi_0(x) + h\psi_1(x) + \mathcal{O}(h^2) \quad (\text{V.A.3})$$

When we substitute this expression into the definition of σ_P (V.2.2) and ρ ((V.2.5) combined with (V.3.4a)) we can also linearize these, whence

$$\sigma_P = \sigma_{P,0} + h\sigma_{P,1} + \mathcal{O}(h^2) \quad (\text{V.A.4a})$$

$$\rho = \rho_0 + h\rho_1 + \mathcal{O}(h^2) \quad (\text{V.A.4b})$$

where the first order quantities are given by

$$\sigma_{P,1} = -2\pi \int_{-1}^1 \psi_1(x) \Delta\psi_0(x) dx \quad (\text{V.A.5a})$$

$$\rho_1 = 64\pi \int_{-1}^1 \int_{-1}^1 S_0(x, x') \psi_0^2(x) \psi_0(x') \psi_1(x') dx dx' \quad (\text{V.A.5b})$$

From the fact that both $\psi(x)$ and $\psi_0(x)$ must be normalized (cf. eq. (V.3.2)) we find that ψ_0 and ψ_1 must be orthogonal

$$\int_{-1}^1 \psi_0(x) \psi_1(x) dx = 0 \quad (\text{V.A.6})$$

Multiplying the zeroth order integrodifferential equation (eq. (V.3.1) with $h=0$) by $\psi_1(x)$, integrating and using the above-mentioned properties yields

$$\sigma_{P,1} + c_{a,0}\rho_1 = 0 \quad (\text{V.A.7})$$

Note that eq. (V.A.1) -when multiplied by $\delta\alpha$ - is a representation of this relationship. Relation (V.A.7) is valid for fixed c or -when calculating the phase transition- for variable c because in both cases eq. (V.A.6) applies. The numerical calculations agree with (V.A.7) for small h.

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SUMMARY

In the first two chapters of this thesis we give an introduction to existing virial theories of rodlike and semiflexible polymers which form a nematic phase when sufficiently concentrated. We compare some recent experiments on stiff polymers with these theories and conclude that in some cases the theories work fairly well. Flexibility plays an important role even for extremely stiff biopolymers like schizophyllan, which can definitely not be considered rodlike in the nematic state. Also the somewhat more flexible polyhexylisocyanate conforms excellently to theory. In the last two years the first systematic studies on concentration and length dependence of the elastic constants of a lyotropic polymer liquid crystal (poly- γ -benzylglutamate) have appeared, which are in partial agreement with theory. However, currently available experiments are sometimes contradictory, which reflects the considerable experimental difficulties and the need of very carefully performed studies.

As an application of virial theory we develop the theory of the elastic constants of rodlike polyelectrolytes in chapter III. For that purpose we employ both a numerical procedure and an analytical method on the basis of asymptotic expansions for a high degree of ordering. Both approaches agree for higher concentrations. Besides a destabilizing twisting effect, the result of charge is to increase the hard-core diameter to a larger effective one. Compared to uncharged rods this has little to no influence on the splay and twist constants, whereas the bend constant increases quadratically with the increase in effective diameter and is also markedly affected by the twisting effect. Finally, the elastic constants for semiflexible polyelectrolytes are derived qualitatively by using the scaling approach for uncharged rods, only incorporating the effective diameter while neglecting the twisting effect.

In chapter IV we carefully reexamine the second virial theory for long semiflexible chains with hard-core interaction. The governing nonlinear integrodifferential equation for the orientational distribution function is transformed to a set of nonlinear algebraic equations, which are solved numerically. Moreover, a bifurcation analysis of the integrodifferential equation is given. We obtain accurate values for the isotropic-nematic phase transition and some properties of the liquid crystal. An important result is the calculation of the so-called global persistence length (the mean distance between consecutive hairpin bends in one single chain in the nematic state) for which we give an exact expression in terms of the orientational distribution function. We show that previous attempts to solve this problem gave incorrect results. We argue that the presence of hairpins strongly affects the splay elastic constant which will depend exponentially on concentration until the chains are completely stretched, where it changes to a linear concentration dependence. We predict that this effect occurs for chains longer than 3.25 times the intrinsic persistence length and should therefore be measurable.

In chapter V we generalize the results of the previous chapter to semiflexible polyelectrolytes. We determine the phase transition, which is on the one hand shifted to lower concentrations by the larger effective diameter but on the other hand destabilized by the twisting effect. Contrary to rodlike polyelectrolytes, it appears that the orientational distribution function at the phase transition does not depend on polyelectrolyte properties or ionic strength. The same applies for properties of the nematic state at the phase transition like the order parameter and global persistence length.

SAMENVATTING

In de eerste twee hoofdstukken van dit proefschrift geven we een inleiding tot de bestaande viriaaltheorieën van staafvormige en semiflexibele polymeren die in oplossing een nematische fase vormen (een zgn. lyotroop polymeer vloeibaar kristal). We vergelijken enkele recente experimenten aan stijve polymeren met deze theorieën en concluderen dat de theorieën in een aantal gevallen vrij goed werken. In vrijwel alle gevallen speelt de flexibiliteit van de macromoleculen een belangrijke rol, zelfs bij extreem stijve biopolymeren zoals schizophyllan, dat in de nematische fase zeker niet als een staaf opgevat kan worden. Ook polyhexylisocyanaat, dat iets flexibeler is, voldoet uitstekend aan de theorie. In de afgelopen twee jaar zijn de eerste systematische experimenten uitgevoerd naar de concentratie- en lengte-afhankelijkheid van de elastische constanten van een lyotroop polymeer vloeibaar kristal (poly- γ -benzylglutamaat). Sommige experimenten zijn echter duidelijk met elkaar in tegenspraak, hetgeen terug te voeren is op problemen bij de uitvoering en interpretatie. Dit onderstreept de behoefte aan zeer zorgvuldig uitgevoerde experimenten.

Als toepassing van deze viriaaltheorieën ontwikkelen we in hoofdstuk III een theorie voor de elastische constanten van staafvormige polyelectrolieten. Daarbij passen we zowel een numerieke methode toe als een analytische op basis van asymptotische expansies voor hoge ordeningsgraad. Beide methoden stemmen voor voldoende hoge concentraties overeen. Naast een destabiliserend draai-effect veroorzaakt de lading een toename van de effectieve diameter van het polyelectroliet. Vergeleken met ongeladen staven heeft dit weinig tot geen invloed op de elastische constanten K_1 en K_2 , terwijl daarentegen de "buig" elastische constante K_3 kwadratisch blijkt af te hangen van de verandering in de effectieve diameter en tevens sterk beïnvloed wordt door het draai-effect. Tenslotte leiden we de elastische constanten van semiflexibele polyelectrolieten kwalitatief af met behulp van een schaaltheorie voor ongeladen staven, waarbij het draai-effect buiten beschouwing wordt gelaten.

In hoofdstuk IV bestuderen we de tweede-viriaaltheorie voor lange semiflexibele ketens met harde interacties. De niet-lineaire integrodifferentiaalvergelijking voor de oriëntatie distributiefunctie wordt omgeschreven tot een stelsel niet-lineaire algebraïsche vergelijkingen, die numeriek opgelost worden. Daarnaast wordt er een bifurcatie-analyse van de integrodifferentiaalvergelijking gegeven. We bepalen nauwkeurige waarden voor de isotroop-nematische fase-overgang en enige eigenschappen van het resulterende vloeibare kristal. Een belangrijk resultaat is de berekening van de zogenaamde globale persistentielengte (de gemiddelde afstand tussen opeenvolgende haarspeldbochten in een keten in de nematische fase), waarvoor we een exacte uitdrukking geven in termen van de oriëntatie distributiefunctie. We tonen aan dat reeds bestaande pogingen om dit probleem op te lossen incorrecte resultaten opleverden. We beargumenteren dat de aanwezigheid van haarspeldbochten grote

invloed heeft op de "spleet" elastische constante K_1 , die daardoor een exponentiële afhankelijkheid van de concentratie zal vertonen totdat de ketens volledig gestrekt zijn, waarna een lineaire concentratie-afhankelijkheid volgt. We voorspellen dat dit effect zal optreden voor ketens langer dan $3.25 \times$ de intrinsieke persistentielengte, zodat het zeker meetbaar moet zijn.

In hoofdstuk V breiden we de resultaten van het voorgaande hoofdstuk uit tot semiflexible polyelectrolieten. We bepalen de fase-overgang, die enerzijds naar lagere concentraties verschuift t.g.v. de grotere effectieve diameter maar anderzijds gedestabiliseerd wordt door het draai-effect. In tegenstelling tot staafvormige polyelectrolieten, blijkt de oriëntatie distributiefunctie voor semiflexibele polyelectrolieten bij de fase-overgang niet af te hangen van de eigenschappen van het polyelectroliet noch van de ionensterkte. Hetzelfde geldt voor eigenschappen van de nematische toestand bij de fase-overgang zoals de orde parameter en de globale persistentielengte.

Curriculum Vitae

Ik ben geboren op 16 juni 1960 te Beverwijk. Na lager onderwijs aan de Zeewijkschool aldaar, doorliep ik het Gymnasium Felisenum te Velsen-Zuid en verkreeg ik het eindexamen VWO-B in 1978. Hierna begon ik met de scheikunde-studie aan de Rijksuniversiteit te Leiden. Op 13 februari 1981 behaalde ik het kandidaatsexamen S3 (hoofdvakken scheikunde en natuurkunde, bijvak wiskunde). Tijdens mijn doctoraalstudie verrichtte ik hoofdvakonderzoek aan de resonantie Raman verstrooiing van kortlevende molekulen in de groep van Dr. C.A.G.O. Varma (Theoretische Organische Chemie) en volgde ik colleges voor mijn bijvakken Theoretische Natuurkunde (Prof.Dr. P. Mazur) en Muziekgeschiedenis (Dr. J. van Biezen en Prof.Dr. J. van der Veen). Ik legde het doctoraalexamen op 27 januari 1984 cum laude af.

Per 1 april 1984 kreeg ik een aanstelling als wetenschappelijk assistent in de vakgroep Fysische en Macromoleculaire Chemie in Leiden voor een promotie-onderzoek o.l.v. Dr. T. Odijk en Prof.Dr. D. Bedeaux aan de theorie van elektrokinetische verschijnselen in oplossingen van polyelectrolyten. Tevens assisteerde ik bij onderwijs voor de werkgroep Chemie en Samenleving. Door de grote problemen die voortvloeiden uit de aard van het gekozen onderzoek, schakelde ik in oktober 1986 over op het onderwerp van dit proefschrift. Door de benoeming van Theo Odijk tot hoogleraar in Delft, wisselde ik vervolgens ook van universiteit en was ik in de periode 1 september 1987 - 1 januari 1989 aangesteld bij de vakgroep Technologie van Macromoleculaire Stoffen aan de Technische Universiteit Delft.

In 1981 ontving ik de Unilever Chemieprijs en in 1982 stelde de Franchimontprijs (RUL) mij in de gelegenheid een zomerschool over "Non-Linear Raman Spectroscopy and its Chemical Applications" te Bad Windsheim (BRD) te bezoeken. Gedurende mijn promotieperiode presenteerde ik mijn onderzoek d.m.v. posters en lezingen op congressen in Herrenalb (European Macromolecular Club, 1985), Den Haag (30th IUPAC International Symposium on Macromolecules, 1985), Saint-Vallier (European Macromolecular Club, 1987), Bordeaux (1st International Conference on Liquid Crystal Polymers, 1987) en New London NH (Gordon Research Conference on Polymer Liquid Crystals, 1988).

Nawoord

Aan het eind van dit proefschrift wil ik graag een aantal betrokkenen bedanken. Allereerst Theo Odijk voor de fijne samenwerking en zijn onovertroffen, inspirerende kennis en inzicht. Daarnaast mijn medepromovendus in Leiden, Paul Venema, voor zijn voortdurende belangstelling en vriendschap en mijn medepromovendus in Delft, Paul van der Schoot, voor het plezierige gezelschap op de TU. Gerard de Vos wil ik hartelijk danken voor het vervaardigen van de tekeningen. En tenslotte: Ronald, bedankt voor alles!