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M. Cates. The anomalous Kerr effect: implications for polyelectrolyte structure. Journal de Physique II, 1992, 2 (5), pp.1109-1119. 10.1051/jp2:1992189 . jpa-00247695

HAL Id: jpa-00247695

<https://hal.science/jpa-00247695>

Submitted on 4 Feb 2008

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Classification
 Physics Abstracts
 61.25H — 61.30G — 87.45

The anomalous Kerr effect: implications for polyelectrolyte structure

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(Received 17 December 1991, accepted 22 January 1992)

Abstract . — In recent experiments on the Kerr effect (electric birefringence) in polyelectrolyte solutions without salt, an anomaly was reported. For a certain intermediate concentration range, the sign of the induced birefringence is opposite to that found at either low or high concentration. An attempt is made to rationalize this data in terms of a locally disc-like clustering of anisometric, polarizable effective particles. If this picture is correct, the birefringence anomaly may help distinguish between competing theoretical models of semidilute polyelectrolyte structure.

1. Introduction.

The structure of semidilute polyelectrolytes, without added salt, remains a matter of theoretical controversy [1-5]. A simple scaling description of salt-free polyelectrolytes is hindered by the fact that six different length scales enter the problem. These are the spacing between charges along the chain, a ; the Bjerrum length $l = e^2/\epsilon k_B T$ (typically 0.7 nm); the chain contour length L ; the Debye length

$$\Lambda = (4\pi CL)^{-1/2} \quad (1)$$

where C is the number of chains per unit volume; the geometrical mesh size or spacing between chains,

$$\xi = C^{-1/3} \quad (2)$$

and the electrostatic persistence length or Odijk length [1]

$$L_e = \Lambda^2/4l. \quad (3)$$

In writing equation (1) for Λ we have assumed strong charging ($a \leq l$) in which case the charge density on the chain is renormalized by condensation until the effective spacing between charges is of order the Bjerrum length l [6]. Equation (1) assumes that only mobile counterions take part in the screening of electrostatic interactions.

Several different concentration regimes can be distinguished. For

$$C \leq C^* \simeq 1/L^3 \quad (4)$$

the chains are fully extended ($L_e \gg L$) but do not overlap ($L \ll \xi$). According to equation (1) the Debye length Λ is *larger* than the interparticle spacing and the chains are strongly coupled, although this result will be modified in practise by a residual amount of salt, or by electrostatic screening by the chains themselves (not included in Eq.(1)). Near the overlap threshold $C \simeq C^*$, the rod length, L , the interparticle spacing ξ and the Debye length Λ are all of the same order of magnitude. The Odijk length L_e is much larger than these and the chains remain stiff.

One can envisage the system near C^* as consisting of slightly soft ellipsoids (or perhaps spherocylinders) at a volume fraction and aspect ratio of order unity (Fig. 1). The roughly ellipsoidal shape comes from the contour where the screened Coulomb interaction between particles is of order $k_B T$. If we set $L = \xi$ to define C^* (say) then equation (1) gives $\Lambda/L \simeq (4\pi)^{-1/2} = 3.5$. Presuming the effective ellipsoids to be of order Λ in radius, their aspect ratio, A_o , is about 2, and their effective volume fraction $\psi \simeq C(4\pi/3)(L/2)^3/A_o^2 \simeq 0.1 - 0.2$. These are crude estimates. Assuming that chains do not become flexible, the scaling $\Lambda \sim C^{-1/2}$ means that if the concentration is increased above C^* , the ellipsoids become more elongated with an aspect ratio

$$A \simeq A_o(C/C^*)^{1/2} \quad (C < \tilde{C}) \quad (5)$$

This varies in such a way that their effective volume fraction $\psi \sim CLA^2$ remains roughly constant as the polymer concentration is increased.

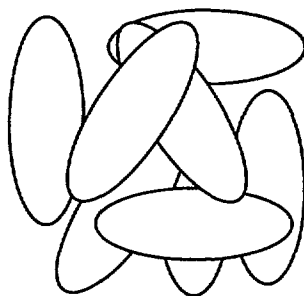


Fig. 1. — A fluid of ellipsoids. Each one represents a polyion backbone with its counterion charge cloud.

There are two basic scenarios for polyelectrolyte structure above C^* . The first, due to Odijk [2] and Hayter *et al.* [3], is that the chains do remain stiff until a second threshold

$$C \simeq \tilde{C} = C^* L / 16\pi l \quad (6)$$

is reached, at which point $L_e \simeq L$, and the aspect ratio (from Eq.(5)) obeys

$$A = A_{\max} \simeq A_o(L/16\pi l)^{1/2} \quad (C \simeq \tilde{C}). \quad (7)$$

Up to this threshold, the picture is one of increasingly thin ellipsoids; it is assumed (with good reason, as discussed in Sect. 4) that there is no long range nematic order. At higher concentrations, $L_e < L$, and the polyions adopt a wormlike structure. One can still envisage an effective ellipsoidal particle (called a "batonnet" in Ref. [3]) although this now represents

the persistence unit of the chain, whose aspect ratio $A \sim \Lambda/L_e$ now becomes a *decreasing* function of concentration:

$$A \sim A_{\max}(C/\tilde{C})^{-1/2} \quad (C > \tilde{C}). \quad (8)$$

Finally at a third concentration threshold

$$C^{**} \sim 0.04(4\pi Ll^2)^{-1}, \quad (9)$$

A becomes of order unity and normal polymer behavior is seen. The corresponding monomer concentration, $C^{**}L/a$, is independent of chain length, and for $a = 0.25$ nm is estimated [2] as about 4×10^{-2} mol l⁻¹.

A second, contrasting model of polyelectrolyte structure above C^* was put forward by Witten and Pincus [5]. They argued that the polyions might bend into a random configuration, not solely as a result of entropy (as assumed in the calculation of L_e), but as a way of reducing the interaction forces between one chain and another. These authors proposed that the persistence length of the chains remained of order ξ for $C \geq C^*$. (This structure is similar to one proposed earlier [4] using different arguments.) The chains are random walks at scales larger than ξ but completely rigid at shorter distances. In this scenario the aspect ratio A of a statistical segment is of order unity (or perhaps A_0) at all concentrations: the intermediate regimes of increasing and then decreasing A are both absent from the description. This model is therefore fundamentally different from the first scenario proposed by Odijk [2] and Hayter *et al.* [3].

The correctness of either picture is still not fully established despite there being a reasonable amount of experimental data from scattering methods [3], viscosity studies [7], etc.. For example in neutron scattering [3], both models predict a peak in the structure factor at $q_{\max} \simeq \pi/\xi$, whereas neither model really explains the viscosity data completely [8].

To help resolve this issue, we consider here recent experimental measurements of the electric birefringence (Kerr effect) of semidilute polyelectrolyte solutions without added salt [9-12]. We argue that the observed behaviour can be qualitatively rationalized, so long as one adopts the Odijk scenario for polyelectrolyte structure above C^* . No similar explanation seems possible within the Witten-Pincus description.

The arguments presented below are qualitative only. (The reason for not presenting more complete calculations is that these are extremely difficult to do.) Previous discussions of the anomaly [9-11, 13] have not led to a consensus on its origin, although there is some conceptual overlap between existing discussions and the picture painted below. This applies particularly to the papers of Krämer, Hoffmann [9] and Thurn [13], though we depart from their treatment at several key points. For example it is argued in reference [9] that rods or ellipsoids cannot be polarized along their long direction at high density because of a type of dielectric breakdown effect. In the present work, we argue instead that a combination of effective steric interactions of the ellipsoids, and strong local field effects, is responsible for the anomalous electric birefringence response.

In referring below to the experimental behaviour, we rely mainly on the detailed data for PSS 400 K (polystyrene sulphonate, $M_w = 400,000$) of reference [9].

2. Electric birefringence anomaly.

Rather than consider the full frequency-dependent problem, we limit attention to the case of a d.c. field applied as a finite pulse. (The usual duration is about 1 ms.) If the pulse is long enough, a steady birefringence Δn is attained. For weak enough fields

$$\Delta n = B\lambda E^2 \quad (10)$$

where B is the Kerr constant, λ the optical wavelength and E the d.c. field strength. Analysis of the time-dependent response can allow the steady birefringence to be resolved into components with different relaxation behaviour.

Since the birefringence signal depends on the polarization of the system at optical frequencies, we can argue that the birefringence is sensitive mainly to the orientation of the *chain backbone* of the polyion. There are in principle two contributions (form and intrinsic birefringence [14]) but for a stiff rod these both amount to a simple difference in the longitudinal and transverse optical polarizabilities, which is independent of concentration but can have either sign. The batonnets in a system above \tilde{C} can presumably also be treated as individual rods for the purposes of this discussion. If so, the usual relation for the birefringence of rods applies in all concentration regimes of interest [14]

$$\Delta n = \beta L \langle u_z u_z - u_x u_x \rangle \quad (11)$$

where β (positive or negative) is a material constant, and the average is taken over the distribution of orientation vectors \mathbf{u} of the rods (or batonnets). Since β does not depend on concentration, Δn is a direct probe of the alignment of the polyions. This alignment is however determined by the *zero frequency* response to a field, which, in contrast to the optical polarizability, should normally be dominated by the charge clouds rather than the chain backbone.

At very high concentrations we expect normal polymeric response, and at very low concentrations the response of noninteracting polyions. In either case, it is well known that the statistical segments or rods should align along the applied field. Indeed it is observed with polyelectrolytes that the sign of B is the same at very high and very low concentrations. However, experimentally it takes the opposite sign at intermediate concentrations [9-11], and according to equation (11) this can only mean that the polyion backbones orient perpendicular to the applied field. The effect went unnoticed for some time [10, 12] since *extremely weak fields* must be used. Indeed, it is very hard to make any measurements at fields low enough to detect the limiting quadratic dependence on E (Eq. (10)). At the lowest fields available, the dependence is less than quadratic. At higher fields, the sign of the response reverts to normal, indicating that rod alignment is again parallel to E [9, 10].

In fact, one can detect (at least) two contributions to the birefringence which have different relaxations [9, 11]. The anomaly is associated with a relatively long relaxation time τ_2 , roughly of order the rotation time of an isolated rod of length L , and quite weakly varying with C . The normal part of the response has relaxation time τ_1 which is similar to τ_2 at low concentrations but *falls* as the concentration is increased. For PSS 400K [9], the anomaly sets in at around $C^* \simeq 0.02 \text{ g l}^{-1}$ and disappears again near $C^{**} \simeq 10 \text{ g l}^{-1}$. These values are estimated theoretically from equations (4,9), with one slight refinement: the stretched chain contour length is that measured for very dilute polyions, rather than the hypothetical value for an all-trans configuration. These differ by a factor of 1.5 [9]. (The value of a must likewise be reduced by a similar factor.)

3. Possible interpretation: polarizable ellipsoids.

The concentration range of the birefringence anomaly does seem to correspond quite closely to the region where anisometric effective particles (ellipsoids, spherocylinders, or batonnets) are predicted to arise within the Odijk framework. But this is not enough. The other main

features that have to be explained are:

- 3.1) the anomalous sign of the steady response;
- 3.2) the disappearance of the anomaly at high field;
- 3.3) the concentration dependence of the relaxation times τ_1 and τ_2 ;
- 3.4) the concentration dependence of the steady response;
- 3.5) the chain length dependence of the steady response.

We argue below that most of these features can be understood *qualitatively* by modelling the system as a set of mutually avoiding ellipsoidal particles of high d.c. polarizability. Each particle represents a polyion (for $C < \tilde{C}$) or batonnet (for $C > \tilde{C}$) with its anisometric counterion cloud. We find that the data can be rationalized quite well if the aspect ratio of the ellipses varies according to the Odijk theory (i.e., Eqs.(5), (7), (8)). In contrast, no similar explanation suggests itself under the Witten-Pincus prediction of a constant aspect ratio $A \simeq A_0 \simeq 1$ for the statistical subunit, throughout the semidilute range. (Note that in both models the effective volume fraction ψ of the effective particles is independent of concentration.)

We now interpret observations 3.1-3.5 in turn within this general picture.

3.1 ANOMALOUS SIGN OF STEADY RESPONSE. — The steady birefringence response of the system at weak enough field are governed by the equilibrium correlations that are present even when the field is switched off [15]. Therefore it is useful to consider these first, starting with a system just above C^* which is modelled as a set of ellipsoids of aspect ratio $A_0 \simeq 3$ (say) and volume fraction $\psi \simeq 0.2$ (at a very crude estimate).

In such a system there should be a strong local coupling between the *orientation* and the *separation* of neighbouring pairs of particles. If the centres of two particles are very close together, then those particles are more likely to be parallel to one another (Fig. 2a). This is found, for example, in hard particle simulations [16]; there may be also some sign of it (at high enough density) in polyelectrolyte simulations using rods of only two charges each [17]. At moderate volume fractions ψ , this steric effect may lead to *disc-like local order* in the fluid of ellipsoids. The effect is present only for rods of reasonable aspect ratio (it disappears in the Onsager limit of $A \rightarrow \infty$) and corresponds to a local *pre-nematic* or (perhaps more precisely) *pre-smectic* clustering (Fig. 2b). There is no particular proof that this type of local ordering exists, but it seems plausible since ellipsoids do show smectic as well as nematic phases. For convenience below we will describe the order in terms of "clusters" of parallel ellipsoids, although as with conventional nematics [18] a smoothly-varying director field might offer a better description. From now on, we assume without further argument that locally disc-like correlations do exist in the unperturbed system.

Since the birefringence response to a very weak field can (in principle) be computed from static correlation functions [15], it might be of interest to calculate the response in, say, a hard-ellipsoid simulation [16]. But unfortunately such simulations do not yet include fluctuating dipole moments on the ellipsoids (i.e., Van der Waals forces) and therefore cannot approximate the linear response of a system of *highly polarizable* ellipsoids in a less polar solvent medium. This is because, for ellipsoids that are highly polarizable, local field effects are always important, however weak the applied field.

Indeed we now argue that, in the presence of local disc-like order, local field effects lead naturally to an alignment of particles transverse to the field, hence explaining the birefringence anomaly. Assuming the field is weak enough to not destroy the equilibrium correlations, the disc-like clusters can (in effect) only rotate as coherent units. Treating each disc as a separate entity, its most polarizable configuration is when E lies in the plane of the disc. Therefore, the

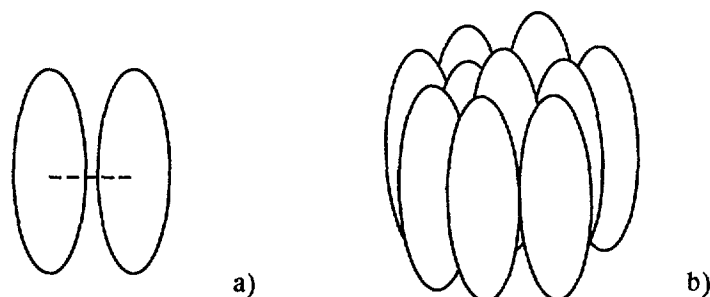


Fig. 2. — a) Strong coupling between orientation and separation of neighbouring particles. The close approach of the centres of mass of the particles precludes some perpendicular orientations and favours parallel ones. The effect is present for two particles but should be stronger at high density. b) Disc-like local cluster of particles, brought about by steric hindrance.

discs will align parallel to the field which means that their component ellipsoids are transversely oriented. The sign of the birefringence, which depends only on the optical response and thus on the alignment of polyion backbones, is accordingly inverted.

The anomalous alignment can also be understood directly in terms of the interactions between the induced dipole moments of the ellipsoids. The local disc-like order means that if the ellipsoids align parallel to the field, each one has a dipole moment that is in a repulsive configuration with respect to its neighbours (Fig. 3a). Conversely, there is an attraction with the ellipsoids transverse (i.e., discs parallel) to the field (Fig.3b). This enhances the macroscopic polarizability in the latter configuration and stabilizes the transverse alignment of the polyions. Hence the polarizable ellipsoid picture plausibly explains the basic finding of an anomalous Kerr effect.

3.2 DISAPPEARANCE OF THE ANOMALY AT HIGH FIELD. — The argument for transverse orientation of ellipsoids remains valid only so long as their local correlations are weakly perturbed by the field. The anomaly will disappear at stronger fields if these disrupt or destroy the tendency to local disc-like order; this will occur if the free energy of the system can thereby be lowered. At high fields the electrostatic part of the free energy will dominate; and this probably can be lowered by adopting a configuration shown in figure 3c in which the disc-like domains are destroyed. This configuration allows the ellipsoids to align with their most polarizable axes along the field, but with much less repulsion between neighbouring dipole moments. For intermediate fields one may have discs aligned with the field, but with the constituent ellipsoids also tilted into the field direction. In this way it should be possible to go continuously from figure 3b to 3c.

Since the anomaly depends on orientation of clusters of many ellipsoids, one expects the corresponding birefringence to saturate very easily. Also, the proposed disc-like order is tenuous and could be disrupted even in a modest field. Therefore, the interacting ellipsoid picture is consistent the observation that departures from equation (10) are observed even at very low fields.

3.3 CONCENTRATION DEPENDENCE OF THE RELAXATION TIMES. — The relaxation time τ_2 of the anomalous response may be the rotational relaxation time or life-time of a disc-like cluster. For PSS 400K [9] this is a few times larger than the rotation time of an isolated rod of length L , suggesting at C^* a disc of rather few ellipsoids. The relaxation time is only weakly

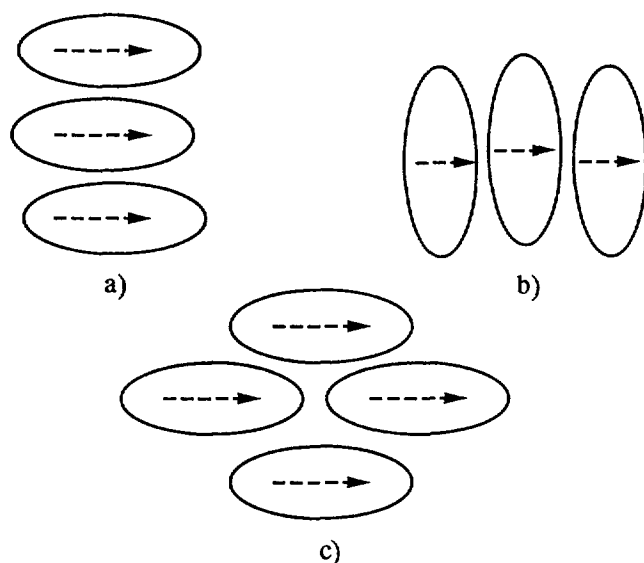


Fig. 3. — a) Conventional alignment by field induces dipoles whose local fields oppose one another. b) Anomalous alignment: the polarizability of each particle is reduced but that of a cluster may be raised, as local field effects are now favourable. c) Disruption of disc-like domains allows normal alignment in strong fields.

dependent on concentration, suggesting that although more ellipsoids are involved at higher C (because they get thinner) the overall size of the cluster is roughly constant. This would not be surprising at least over a limited range, though the model does not explain it directly.

To explain the relaxation time τ_1 of the normal part of the response, one can argue that this corresponds to a “wobble” mode in which an ellipsoid makes angular deflections about its mean direction forced on it by its neighbours. (This mode is also familiar from nematic liquid crystals [18].) This is consistent with the general magnitude of τ_1 reported in reference [9]. It is also consistent with the observed *decreasing* trend as concentration is raised: for concentrations between C^* and \tilde{C} , the ellipsoids are thinner and constrained in a narrower “cage” by their neighbours. Their angular deflections are reduced, and the time-scale for exploring these fluctuations falls accordingly. Roughly one should have $\tau_1 \sim A^{-2} \sim C^{-1}$ in this regime, which is broadly consistent with the data of reference [9]. On the other hand, a more complex behaviour is expected for $C \geq \tilde{C}$ since the batonnets are connected into chains (and their aspect ratio now decreases). This may be why at the upper end of the anomalous range, a slower mode of relaxation for the normal part of the response (denoted τ_3 in Ref. [9]) sets in.

3.4 THE CONCENTRATION DEPENDENCE OF THE STEADY RESPONSE. — This can be rationalized if we assume that the strength of the anomalous part of the response is always an increasing function of the aspect ratio A of the rods or statistical segments. (This is reasonable although it might fail if A became extremely large, since the tendency to disc-like rather than simply nematic local order may be reduced in this limit.) If so, according to equations (5-8), we predict the following features:

- (i) The anomaly should extend roughly from C^* to C^{**} . As mentioned previously, this is roughly true for the PSS 400K system of reference [9].

- (ii) Since $A \sim (C/\tilde{C})^{1/2}$ for $C \leq \tilde{C}$ and $A \sim (C/\tilde{C})^{-1/2}$ for $C \geq \tilde{C}$, then regardless of the details of how the response depends on A (so long as it is an increasing function) one expects a broadly symmetrical peak in the anomalous response if the birefringence B at some fixed field is plotted against $\log C$. This is indeed the case for the PSS 400K system as can be seen from figure 2 of reference [9].
- (iii) On the other hand, if the response at fixed field is plotted against C directly, rather than $\log C$, an extremely asymmetric maximum should arise. The maximum response should be near \tilde{C} which obeys (from Eqs. (6, 9))

$$\tilde{C} \simeq (25C^*C^{**}/64\pi)^{1/2} \quad (12)$$

A rough and ready comparison, which can be made without any independent measurement of C^* , \tilde{C} and C^{**} is as follows. We can gauge the onset and the disappearance of the anomaly at low and high concentrations respectively by the two concentrations C_1 and C_2 at which B changes sign. If we assume these are close to C^* and C^{**} respectively, then according to equation (12), the *maximum* response should be at a concentration C_{\max} close to

$$C_3 = (C_1C_2)^{1/2} \quad (13)$$

Since for high molecular weight polyions C_1 and C_2 may differ by a large factor (roughly 100 for PSS 400K) this is a nontrivial test.

A plot of B against C for PSS 400K at a field strength of $5 \times 10^4 \text{ V m}^{-1}$ is shown in figure 4, with the values of C_1 , C_2 and C_3 indicated. As can be seen, the maximum of B is very close to C_3 in agreement with equations (12) and (13). The very precise agreement is rather fortuitous (for example, a numerical factor was dropped between Eq. (12) and Eq. (13)). Also, the agreement at the lowest field strength measured ($2.5 \times 10^4 \text{ V m}^{-1}$) is not quite as good. Nonetheless, the basic trend seems to be consistent with the prediction.

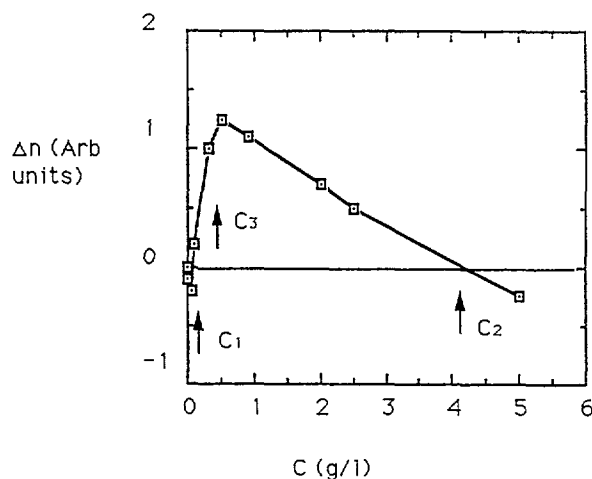


Fig. 4. — Graph of birefringence against polyelectrolyte concentration for PSS 400K. Data from reference [9].

A closer comparison of the theoretical and experimental quantities for the same system is shown in table I. Theoretical values assume $L = 320$ nm and $a = 0.15$ nm. (As previously discussed (Sect. 2) these take account of the observed end-to-end length of the chains in dilute solution rather than the fully extended length.) The agreement is far from perfect, but again close enough to suggest that the interacting ellipsoid picture may be reasonable.

Table I. — *Comparison of theoretical with experimental quantities for PSS 400 K. (C: g/l).*

Theory	Experiment
$C^* = 0.02$	$C_1 = 0.04$
$C^\sim = 0.2$	$C_{\max} = 0.4 - 1.0$ (depends on E)
$C^{**} = 14$	$C_2 = 4$
$(C^* C^{**})^{1/2} = 0.5$	$C_3 = (C_1 C_2)^{1/2} = 0.4$

3.5 THE CHAIN LENGTH DEPENDENCE OF THE STEADY RESPONSE. — We have emphasized the data for one particular molecular weight, but obviously to check the picture the dependence on chain length must also be understood. Theoretically this enters through the values of C^* and \tilde{C} ; according to equation (7) the maximum aspect ratio therefore also depends on L .

Some preliminary description of the behaviour of higher (1200,000) molecular weight PSS samples is given in reference [9]. However, the measured end-to-end distance in dilute solution is scarcely larger than that for PSS 400K. This suggests either that the behaviour of polyelectrolytes for $C < C^*$ is after all not understood [19], or that there is some residual ionic strength present which means that the system is effectively not salt-free at low concentrations. Hence we do not discuss this data here.

An interesting question which does arise for higher molecular weights is whether a nematic phase should be present. As emphasised by Witten and Pincus [5], such a phase might well be expected if the polyions remain stiff. However, the various order unity factors in the Odijk model (which are themselves uncertain to within, say, factors of 2), seem to conspire against this. For example from our rough estimate of $A_0 = 2$ and equation (7) we have for PSS 400K an estimate $A_{\max} \simeq 6$ for the largest aspect ratio achieved within the Odijk picture. Since $A_{\max} \propto L^{1/2}$ (from Eq. (7)) we find for PSS

$$A_{\max} \sim 6(M_w/400,000)^{1/2} \quad (14)$$

If our crude estimate of the ellipsoid volume fraction is also correct ($\psi = 0.2$) then certainly one could not expect nematic order for A less than about 30. To obtain this value for A_{\max} would require $M_w \simeq 10^7$. The ionic strength at \tilde{C} is then no more than about 10^{-5} mol l $^{-1}$, so to observe a nematic phase would require careful dialysis of ionic impurities. It is even possible (given the uncertainty in our numbers) that the background ionic strength of pure water (2×10^{-7}) is enough to prevent a nematic phase. Similar arguments for the absence of nematic order were given by Hayter *et al.* [3]

Finally, we consider shorter chains. Data for PSS 100K is also reported in reference [9] ($L \simeq 80$ nm), and the birefringence anomaly has also been found in charged surfactant micelles

($L \simeq 40$ nm) [13]. For the micelles there are several complicating factors (the micelle size can grow at high concentrations; also there may be local stiffness of non-electrostatic origin), but we ignore these here. The main difference between these systems and PSS 400K is that the anomaly arises in a much narrower concentration range. Theoretically, from equations (4,9), the "width" W of the anomaly may be estimated as

$$W = C_2/C_1 \simeq C^{**}/C^* \propto L^2 \quad (15)$$

Taking the experimental value of $W \simeq 100$ for PSS 400K, we predict roughly $W \simeq 6$ for PSS 100K and $W \simeq 1.5$ for micelles of length 40 nm. These are broadly consistent with the data [13, 9]. These results show that quite large molecular weights are needed before the threshold concentrations C^* , \tilde{C} and C^{**} become well separated, allowing an analysis such as that of figure 4 to make sense.

4. Conclusion.

We have proposed a tentative interpretation of the electric birefringence anomaly in polyelectrolyte based on Odijk's model of semidilute polyelectrolyte structure. For the PSS 400K system of reference [9], the data seems broadly consistent with this picture in several different respects. More detailed experimental work on the anomalous electric birefringence for high and very high molecular weight materials (at very low ionic strengths) might be very helpful in clarifying the situation. It would also be interesting to see experiments on uncharged colloidal particles of ellipsoidal or spherocylindrical shape. According to our explanation, these should also have an anomalous birefringence at high volume fractions, so long as the ellipses have very different polarizability from that of the solvent.

On the theoretical side, simulations of ellipsoids or spherocylinders with fluctuating dipolar forces would be useful. (These would obviously be interesting also in modelling true colloidal particles as mentioned above.) However, such simulations are probably difficult to do. Likewise direct simulations of polyion systems are in their infancy [17]. There are also integral equation theories in both cases, but in few of these is the local coupling between angular and translational degrees of freedom accurately treated [17]. Therefore it may be some time before the qualitative arguments given in this paper can be confirmed or rejected in the light of a more rigorous theory.

Acknowledgements.

I am grateful to M. Allen, T. J. Drye, H. Hoffmann, J.-F. Joanny, P. Pincus, S. Safran for valuable discussions. This work was funded in part under EC Grant SC1-0288 C.

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