

Amplification of chirality in helical supramolecular polymers beyond the long-chain limit

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The optical activity of helical homopolymers devoid of chiral centers increases drastically when a small amount of homochiral monomers is incorporated into them. We study this so-called sergeants-and-soldiers effect of chirality amplification in solutions of helical supramolecular polymers with a theoretical model that bears a strong resemblance to a one-dimensional, two-component Ising model. In the limit of very long self-assembled helical polymers, the strength of the sergeants-and-soldiers effect depends strongly on the free energy of a helix reversal and less so on the concentration of aggregating material. Outside the long-chain limit, we find the reverse—that is, a strong concentration dependence and a weak dependence on the helix-reversal energy. Our treatment gives an excellent agreement with recently published circular-dichroism measurements on mixed aggregates of discotic molecules in the solvents water and *n*-butanol, at two different overall concentrations. © 2004 American Institute of Physics. [DOI: 10.1063/1.1689645]

I. INTRODUCTION

Many biological and synthetic molecules polymerize into helical chains.¹ In mixtures of homochiral and achiral versions of such materials, the polymers formed typically display a larger Cotton effect than one may expect from the fraction of chiral material they contain.^{2,3} This so-called sergeants-and-soldiers type of chirality amplification⁴ is due to a cooperative shift in the balance between the numbers of right-handed and left-handed helical bonds, caused by the influence the chiral monomers have on the conformation of nearby achiral monomers. The effect has been observed both in conventional polymers,^{2,4–7} which have a fixed length and composition, and in supramolecular polymers,^{8–10} which are polymerlike aggregates formed through the linear self-assembly of monomeric units. For the latter type of polymer the length and composition are equilibrium properties. That a strong sergeants-and-soldiers effect is indeed observed in the latter system is quite remarkable because supramolecular polymers are in a way fragile, involving relatively weak, reversible bonds between the monomeric units. Note that whenever we use the term “bond” in this paper, we refer to this type of reversible physical interaction between monomers (e.g., through solvophobic interactions, hydrogen bonding, and so forth), and not to conventional chemical bonds, unless explicitly mentioned.

The sergeants-and-soldiers principle in conventional polymers has been studied theoretically by several authors.^{11–13} (For a recent review paper on this topic, see Ref. 3). From these treatments it becomes clear that the strength of the chirality amplification depends strongly on the free-energy penalty of a helix reversal and on the degree of polymerization. In the long-chain limit the dependence on

the chain length disappears,^{3,12} and the strength of the chirality amplification depends only on the free energy of the helix reversal. The larger this free-energy penalty, the larger the number of achiral monomers that are affected by the insertion of a single homochiral monomer, and the stronger the chirality amplification.

The sergeants-and-soldiers effect has only recently been discovered in supramolecular polymers,^{8–10} and attempts to describe it theoretically have been few in number.^{10,14} The usefulness of these treatments is limited, however, as they are either valid only in the long-chain regime¹⁴ or invoke a mean-field approximation that is difficult to justify due to the essentially one-dimensional character of the problem.¹⁰ In this paper we outline a phenomenological approach that improves upon the earlier work by describing the sergeants-and-soldiers principle in supramolecular polymers beyond the long-chain limit and outside of the mean-field approximation as regards the configurational statistics of the chains. The model we apply, while idealized, captures the essential physics of the system. We predict, in accordance with recent experimental measurements^{8,9} and contrary to what is known for conventional polymers, that there are (at least) two regimes: one where the chirality amplification depends on the overall monomer concentration and one where this is not so. We argue that, because the mean degree of polymerization of supramolecular polymers is roughly proportional to the square root of the solute concentration,^{15–18} the concentration dependence of the chirality amplification in this type of polymer is actually a chain-length dependence similar to that found in conventional polymers. The problem in hand should therefore be accurately described by combining the usual theory of equilibrium polymerization with a non-mean-field description of the conformational state of the polymers. Comparison with experimental results shows that our treatment is indeed a sensible one. For the long-chain limit, we

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recover the result obtained in Ref. 14 and predict that outside of this limit the sergeants-and-soldiers effect becomes more strongly dependent on the concentration and less so on the free-energy cost of a helix reversal.

The remainder of this paper is organized as follows. In Sec. II we outline a model that describes chirality amplification in a helical chain, based on the two-component Ising chain, and calculate the partition function of such a chain. In Sec. III, we apply this partition function in the classical theory of equilibrium polymerization and derive a formal expression for the average difference between the number of right-handed and left-handed helical bonds per unit mass (the so-called mean net helicity) as a function of the overall concentration of solute molecules, the free energy of aggregation, the fraction of homochiral monomers, and the free-energy cost of a helix reversal. Next, in Sec. IV, we show how the mean net helicity responds to changes in these parameters and discuss the various regimes and trends that appear. Here we focus on the dependence of the net helicity on the solute concentration and on the free-energy penalty of a helix reversal. In Sec. V, we compare our results to those obtained from circular-dichroism measurements on mixtures of chiral and achiral discotic molecules in the solvents *n*-butanol and water.^{8,9} The agreement between our theory and these experiments is quite good. Finally, in Sec. VI, we present our conclusions.

II. SINGLE-AGGREGATE PARTITION FUNCTION

We consider a dilute solution of polydisperse aggregates that we presume to be rod like, so that we may ignore both interaggregate and long-ranged intra-aggregate interactions. The aggregates consist of two types of monomer: homochiral and achiral. Of course, the actual interaction between the monomers and conformational state of the aggregates depends on many factors, from the chemical architecture to the solvent properties. In our approach, we implicitly deal with these contributions by introducing several free-energy parameters. This is discussed in more detail below.

If we assume that the direct interactions along the main axis of an aggregate are short ranged, we can describe the conformational state of this aggregate with a one-dimensional, two-component Ising model.^{19–22} We treat the bonds between monomers as spins that can have a value of ± 1 , corresponding to a right- or left-handed screw sense. Given the strong preference of chiral molecules for a certain helical handedness, we force any bond following a chiral molecule to have a fixed spin value of $+1$.

Obviously, the free-energy penalty of a “down” spin (with a spin value of -1) following a chiral monomer can also be given a finite value, rather than being fixed at infinity as we do here. However, this would introduce an additional parameter in our model that somehow needs to be fixed in any comparison to experiment. This is problematic for a number of reasons,¹⁴ the most important one being that it can be shown to merely renormalize other parameters we already use in our description, at least in the double limit where the cooperativity is high and moreover the additional energetic parameter exceeds the free energy of a helix reversal, which is the most interesting regime. As we argued in previous

work, it suffices to fix the bond type following a chiral molecule to describe the essential physics of the problem. In effect, we ignore helix reversals in all-chiral aggregates.¹⁴

Let N denote the number of monomers that comprise the aggregate. In accordance with the above arguments, our model Hamiltonian reads¹⁴

$$H = \frac{1}{4} R \sum_{i=1}^{N-2} \left(-\frac{n_i+1}{s_i+n_i} \frac{n_{i+1}+1}{s_{i+1}+n_{i+1}} + 1 \right)^2 + \frac{1}{2} P \sum_{i=1}^{N-1} \left(\frac{n_i+1}{s_i+n_i} + 1 \right) - E(N-1) \quad (1)$$

provided $N \geq 3$. For $N=1$, we have $H \equiv 0$, whereas $H = \frac{1}{2} P[(n_1+1)/(s_1+n_1)+1] - E$ for $N=2$. In Eq. (1), $s_i = \pm 1$ gives the state of the i th spin along the chain and n_i describes the chirality of the i th monomer, with $n_i=0$ for an achiral monomer and $n_i=1$ for a chiral one. The parameter $R \geq 0$ is the usual coupling constant between neighboring spins, which corresponds to the free-energy penalty on a helix reversal between achiral monomers. That such a helix reversal should be unfavorable can easily be imagined from steric arguments: a monomer involved in a right-handed bond on one side and a left-handed bond on the other would have a conformation that does not correspond to either of these stable conformations: i.e., this would ultimately lead to a frustrated conformational state. The quantity P is in Ising terms the dimensionless magnetic-field strength and represents the excess free energy associated with a bond of one handedness over the other. This free energy only has a value different from zero if the formation of bonds with one screw sense is biased, i.e., by the addition of a chiral solvent or by the use of an external field which couples to the screw senses in a different way. We shall set this free energy equal to zero later, but introduce it here in order to be able to calculate the fractions of both types of helical bond. The bare energy of a bond we set equal to $-E$; it determines the *a priori* propensity of the monomers to form aggregates. (These free energies and, indeed, all energies in this paper are given in units $k_B T$.) Note that the Hamiltonian, Eq. (1), is constructed in such a way that any configuration that contains a spin i with a value of $s_i = -1$ following a chiral molecule ($n_i=1$) is completely suppressed. The propensity for the formation of a bond, the bias toward a certain screw sense, and the likelihood of helix reversal (and hence all three energy scales we introduced) depend on the geometry of the monomers, as well as on the solvent properties. Here we obviously treat all parameters phenomenologically.

From the Hamiltonian, Eq. (1), we can formally write down the quasi-grand partition function of an aggregate, in which the composition of the aggregate can change, but its total length is fixed at N monomers, as

$$\Xi(N) = \left(\prod_{k=1}^N \sum_{n_k=0,1} \right) \exp \left[\mu_0 \left(N - \sum_{i=1}^N n_i \right) + \mu_1 \sum_{i=1}^N n_i \right] \times \left(\prod_{j=1}^{N-1} \sum_{s_j=\pm 1} \right) \exp(-H). \quad (2)$$

Here the two bracketed terms in front of the exponentials denote repeated sums and μ_0 and μ_1 in the exponential are the chemical potentials of the achiral and chiral molecules. The transfer matrix method presents an elegant way to simplify the partition function, Eq. (2),¹ giving

$$\Xi(N) = \left(\prod_{k=1}^N \sum_{n_k=0,1} \right) \exp \left[\mu_0 \left(N - \sum_{i=1}^N n_i \right) + \mu_1 \sum_{i=1}^N n_i \right] \times \left(\mathbf{u} \cdot \prod_{i=2}^{N-1} \mathbf{M}_{n_i} \cdot \mathbf{u}^\dagger \right) \exp[E(N-1)]. \quad (3)$$

The matrix \mathbf{M}_{n_i} contains the (unnormalized) probabilities that a particular type of bond follows another bond along the chain. For our two-component system, we define two matrices \mathbf{M}_0 and \mathbf{M}_1 , one to describe the statistical weights for a bond following an achiral monomer and one to describe those for a bond following a chiral one. Note that the first bond of the aggregate is not included in the matrix multiplication, as it does not follow a preceding bond. This bond is instead described by the end vector \mathbf{u}^\dagger , while \mathbf{u} describes the other aggregate end; \mathbf{u}^\dagger and \mathbf{u} depend on the boundary conditions imposed.²³

The statistical weights for the matrices \mathbf{M}_0 and \mathbf{M}_1 can be obtained from Eq. (1) by standard methodology.²⁴ They read

$$\mathbf{M}_0 = \begin{pmatrix} 1 & \sqrt{\sigma} \\ \sqrt{\sigma}s & s \end{pmatrix}, \quad \mathbf{M}_1 = \begin{pmatrix} 0 & 0 \\ \sqrt{\sigma}s & s \end{pmatrix}. \quad (4)$$

Here $s \equiv \exp(-P)$ is the Boltzmann factor of a spin with value +1 over one with a value -1 and $\sigma \equiv \exp(-2R)$ is the square of the Boltzmann factor of a spin (or helix) reversal, both of which are taken to be independent of the type of monomer present. (Below, we make a distinction between the different types of monomer, based on their packing in the aggregates and the resulting difference in their contribution to the optical properties of the solution.) The latter can be seen as a measure for the cooperativity of the chirality amplification: the lower σ , the larger the number of achiral monomers that are affected by a single chiral monomer and the longer the mean distance between helix reversals. (Note that the quantities s and σ have similar meanings as in the well-known theory of Zimm and Bragg for the helix-coil transition in polymers.²⁵)

Further simplification is possible, if we define an excess chemical potential $\mu \equiv \mu_1 - \mu_0$ that couples to the chiral content and a reference chemical potential μ_0 that couples to the total mass incorporated into assemblies. Equation (3) then simplifies to

$$\Xi(N) = \exp[\mu_0 N + E(N-1)] \tilde{\mathbf{u}} \cdot \mathbf{M}^{N-2} \cdot \tilde{\mathbf{u}}^\dagger, \quad (5)$$

which can be obtained by absorbing the excess-chemical-potential term into \mathbf{M}_{n_i} , factorizing the summations, and evaluating each term separately. \mathbf{M} is the sum of the contributions of chiral and achiral monomers, and reads

$$\mathbf{M} = \mathbf{M}_0 + z\mathbf{M}_1 = \begin{pmatrix} 1 & \sqrt{\sigma} \\ \sqrt{\sigma}s(1+z) & s(1+z) \end{pmatrix} \equiv \begin{pmatrix} 1 & \sqrt{\sigma} \\ \sqrt{\sigma}s' & s' \end{pmatrix}, \quad (6)$$

where $z \equiv \exp(\mu)$ is a fugacity linked to the total amount of chiral material in the solution and $s' \equiv (1+z)s$ can be loosely labeled as the overall preference for one handedness over the other in a mixed aggregate. Note that the factor z is present for each chiral monomer and, as such, can be used to determine the number of these monomers in an aggregate. For the end vectors $\tilde{\mathbf{u}}$ and $\tilde{\mathbf{u}}^\dagger$ we write

$$\tilde{\mathbf{u}} = (1+z, \quad 1+z), \quad \tilde{\mathbf{u}}^\dagger = \begin{pmatrix} 1 \\ s' \end{pmatrix}, \quad (7)$$

assuming free ends; we do not enforce a restriction to a particular conformation for the aggregate ends, because there is no reason to assume that either aggregate end will prefer a right- or left-handed helical conformation.²³ Note also that, upon going from \mathbf{u}^\dagger to $\tilde{\mathbf{u}}^\dagger$ (and \mathbf{u} to $\tilde{\mathbf{u}}$), we have absorbed the term from Eq. (3) describing the chemical potential of the first and last monomers of the chain into the end vectors.

The partition function can now be calculated by matrix multiplication and takes the form

$$\Xi(N) = \frac{z_0^N (1+z) \exp(-E)}{(\lambda_+ - \lambda_-) \sqrt{\sigma}} [(\lambda_+ - 1 + \sqrt{\sigma}) \times (1 - \lambda_- + s' \sqrt{\sigma}) \lambda_+^{N-2} + (\lambda_- - 1 + \sqrt{\sigma}) \times (\lambda_+ - 1 - s' \sqrt{\sigma}) \lambda_-^{N-2}]. \quad (8)$$

Here $z_0 \equiv \exp(\mu_0 + E)$ is again a fugacity, and $\lambda_\pm = \frac{1}{2} + \frac{1}{2}s' \pm \frac{1}{2}\sqrt{(s'-1)^2 + 4\sigma s'}$ are the eigenvalues of the transfer matrix. Strictly speaking, this partition function is only valid for $N > 2$: however, inserting $N=2$ gives the correct result $\Xi(2) = z_0^2 \exp[-E(1+z)(1+s')]$. For $N=1$, we put $\Xi(1) \equiv z_0(1+z) \exp(-E)$. In earlier work,¹⁴ we discarded the contribution proportional to λ_-^{N-2} and, in doing so, neglected finite-size effects; this reduces the partition function to a single term, which greatly facilitates further calculations. Here we keep both terms, since we are interested in the influence of finite-size effects on the chirality amplification. We may simplify Eq. (8) by noting that, by symmetry, a right- and left-handed bond are equally likely for the achiral species in the absence of an external bias and set $s=1$ and, thus, $s'=1+z$. However, for reasons to become clear in the next section, we choose not to do this yet.

Note that the model we use is not symmetrical—i.e., that a bond following a chiral monomer is treated differently from one preceding the same monomer. We feel it is justified to use this model, however, since a helix is inherently directional and is, therefore, an asymmetrical structure. Nonetheless, it is easy to adapt our model to enforce symmetry between bonds preceding and following a chiral monomer: instead of forbidding only “down” spins following a chiral monomer, we then also forbid the occurrence of a helix reversal at this monomer. In that case both the

bonds before and after the chiral monomer must be in the same configurational state—i.e., “up.” This changes the transfer matrix \mathbf{M} to

$$\mathbf{M} = \begin{pmatrix} 1 & \sqrt{\sigma} \\ \sqrt{\sigma}s & s \end{pmatrix} + z \begin{pmatrix} 0 & 0 \\ 0 & s \end{pmatrix} = \begin{pmatrix} 1 & \sqrt{\sigma} \\ \sqrt{\sigma}s & s(1+z) \end{pmatrix}. \quad (9)$$

This adjustment of the theory turns out not to give any significant change in the results for the chirality amplification, at least for small σ . Since the small- σ regime is of the most interest to us, we consider it justified to use the theory as derived above.

III. MEAN NET HELICITY OF A SOLUTION OF AGGREGATES

Now that we have established the partition function of a single aggregate, let us investigate how this affects the mean net helicity of a solution of polydisperse, self-assembled aggregates. This net helicity can be measured experimentally, at least in principle. It expresses itself as an optical activity. As we shall discuss in some more detail in Sec. V, however, there are more factors than can have a contribution to the overall optical activity of a solution, as the optical activity reflects the overall chirality of the solution.

From the theory of equilibrium polymerization^{15–17} we can find that, within a saddle-point approximation for the size distribution of the aggregates, the grand potential per unit volume of a solution of self-assembled polymers reads

$$\Delta\Omega = \sum_{N=1}^{\infty} \rho(N) [\ln \rho(N) - 1 - \ln \Xi(N)]. \quad (10)$$

Here $\rho(N)$ is the number density of aggregates of size N , made dimensionless by multiplying it by the volume of a monomer (there are no other length scales in our coarse-grained model). The equilibrium size distribution can be calculated by minimizing $\Delta\Omega$ with respect to $\rho(N)$. This gives

$$\rho(N) = \Xi(N). \quad (11)$$

Using the equilibrium size distribution, we can calculate the mean net helicity, defined as the difference between the number of right- and left-handed helical bonds averaged over all monomers present in the aggregated state:²⁶

$$\begin{aligned} \langle \eta \rangle &= \langle \theta_+ \rangle - \langle \theta_- \rangle \\ &= -1 + \frac{2}{\phi - \rho(1)} \sum_{N=2}^{\infty} \rho(N) \frac{N}{(N-1)} \frac{\partial \ln \Xi(N)}{\partial \ln s'}, \end{aligned} \quad (12)$$

with $\langle \theta_+ \rangle$ and $\langle \theta_- \rangle$ the mean fractions of right- and left-handed helical bonds, and ϕ the total volume fraction of aggregating molecules,

$$\phi = \sum_{N=1}^{\infty} N \rho(N), \quad (13)$$

which we keep constant. Note that monomers are not taken into account in this definition, because they contain no bonds. The overall fraction of chiral monomers in the solution can be calculated from

$$x \equiv \frac{1}{\phi} \sum_{N=1}^{\infty} \rho(N) \frac{\partial \ln \Xi(N)}{\partial \ln z}, \quad (14)$$

and the mean aggregate size is defined as

$$\langle N \rangle \equiv \frac{\phi}{\sum_{N=1}^{\infty} \rho(N)}. \quad (15)$$

We now plausibly assume, as discussed earlier, that achiral monomers have no preference for a left- or right-handed conformation and set $s' = 1 + z$ —i.e., $s = 1$. This reduces the eigenvalues of the transfer matrix \mathbf{M} to

$$\lambda_{\pm} = 1 + \frac{1}{2} \pm \frac{1}{2} \sqrt{z^2 + 4\sigma(1+z)}. \quad (16)$$

After this substitution is made, we can express the mean net helicity in terms of z , σ , ϕ , E , and μ_0 using Eqs. (8) and (11)–(13).

To determine the mean net helicity as a function of the fraction chiral material, we fix z and numerically determine the value of the fugacity z_0 by inserting Eqs. (8) and (11) into Eq. (13), performing the sum, and solving the resulting equation for a fixed value of the dimensionless quantity $\phi \exp(E)$. Here $-E$ and ϕ are the earlier-introduced bare bond energy and the overall volume fraction of aggregating molecules. This gives six possible solutions for z_0 . To determine which is the physically relevant one, we take into account the following. First, since μ_0 and E are real numbers, z_0 must be non-negative and real. Second, for the sum in Eq. (13) to converge, $z_0 \lambda_+$ must be smaller than 1 for all compositions of the polymers. This means that $z_0 < 1$, since $\lambda_+ \geq 1$. In all the cases we investigated, this reduces the number of physically relevant solutions to 1. With σ , z_0 , and z known, we can now calculate the mean net helicity and the corresponding fraction of chiral material by simple insertion. The entire “magnetization” or helicity diagram, giving $\langle \eta \rangle$ as a function of the fraction of chiral material x , can be obtained by using different values of z and repeating the calculation.

IV. RESULTS

In Ref. 14 we showed that, provided the supramolecular polymers are very long, the strength of the sergeants-and-soldiers effect is strongly dependent on the value of the cooperativity parameter σ (and hence on the free energy of a helix reversal) and independent of the concentration of assembling molecules. As we show next, for chains that are not very long, the reverse is true and the net helicity does become a function of the overall volume fraction of assembling monomers ϕ .

We identify three regimes: one where the chains are long, one where the chains are in some sense short, and a monomeric regime where the concept of chirality amplification becomes meaningless. It turns out that a natural way to quantify and distinguish these regimes is by considering not the mean aggregation number $\langle N \rangle$, but one scaled to a correlation length, so that one counts the number of correlation lengths in an aggregate, rather than the number of monomers.

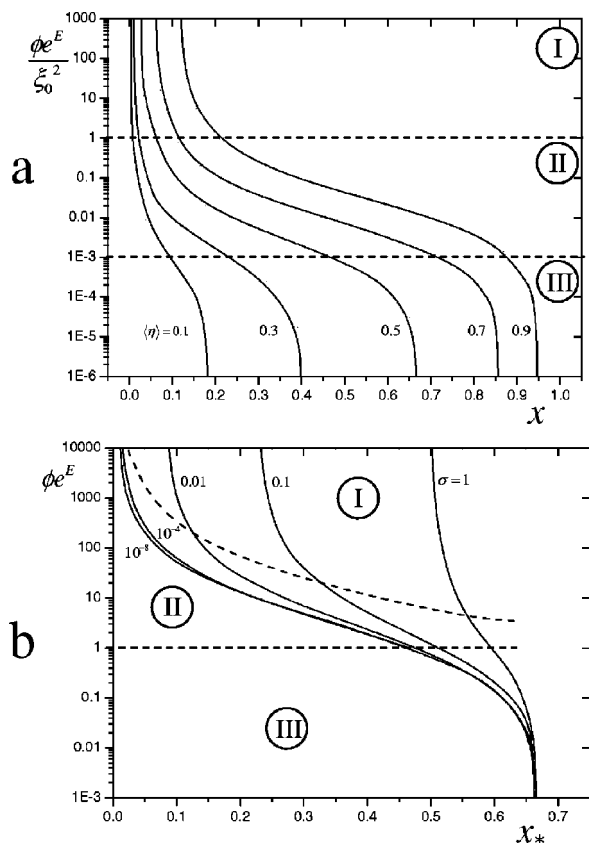


FIG. 1. (a) Mass action parameter $\xi_0^{-2} \phi \exp E$ versus the fraction of chiral material x , for $\sigma = 10^{-3}$. The lines indicate those values of x and $\xi_0^{-2} \phi \exp E$ that produce values of a net mean helicity of $\langle \eta \rangle = 0.1, 0.3, 0.5, 0.7$, and 0.9 , as indicated. The Roman numbers I, II, and III indicate the long-chain regime, the short-chain regime, and the monomer regime, separated by dashed lines. (b) $\phi \exp E$ as a function of the fraction of chiral material corresponding to a net helicity of one-half its maximum value, x_* . The lines indicate the values of x_* and $\phi \exp E$ for different values of σ , as indicated. The Roman numbers and dashed lines again indicate the regimes, as in (a).

Let ξ_0 denote the “bare” correlation length—i.e., the mean distance between helix reversals in an infinite aggregate that does not contain any chiral material. (Obviously, the actual correlation length depends on the aggregation number and the chiral content of the chain.) This bare correlation length is given by $\xi_0 \equiv (-\partial \ln \lambda_+ / \partial R)^{-1}$, with $\lambda_+ = 1 + \frac{1}{2}z + \frac{1}{2}\sqrt{z^2 + 4\sigma(1+z)}$ the largest eigenvalue of the transfer matrix: cf. Eq. (8). We find $\xi_0 = 1 + \sigma^{-1/2}$, which reduces to $\xi_0 \approx \sigma^{-1/2}$ if $\sigma \ll 1$ —i.e., if the cooperativity is high. The relevant control parameter determining the relative size of the assemblies is now $\xi_0^{-2} \phi \exp(E)$, since the “bare” degree of polymerization obeys $\langle N \rangle_0 = \frac{1}{2} + \frac{1}{2}\sqrt{1 + 4\phi \exp(E)}$ $\sim \sqrt{\phi \exp(E)}$, at least for $\langle N \rangle \gg 1$ (Ref. 18). Here the bare degree of polymerization is defined as the mean number of monomers of an all-chiral aggregate. As we shall see below, $\langle N \rangle \approx \langle N \rangle_0$; i.e., the actual degree of polymerization is quite close to the bare one, meaning that the presence of a second type of monomer does not significantly affect the mean aggregate size.

In Fig. 1(a) we plot curves of constant mean net helicity $\langle \eta \rangle = 0.1, 0.3, 0.5, 0.7$, and 0.9 as a function of the control parameter $\xi_0^{-2} \phi \exp(E)$ and the fraction of chiral material x ,

for a fixed degree of cooperativity $\sigma = 10^{-3}$. Three regimes can be distinguished, indicated with Roman numerals in the figure. These are (I) the “long-chain regime,” where $\phi \exp(E) \geq \xi_0^2$, (II) the “short-chain regime,” where $1 \leq \phi \exp(E) \leq \xi_0^2$, and (III) the “monomer regime,” for which $\phi \exp(E) \leq 1$. In the long-chain regime the sergeants-and-soldiers effect is (virtually) independent of the concentration: the curves become vertical in this regime. In the short-chain regime there is a strong decrease in the chirality amplification as the concentration decreases, because the relative amount of chiral material needed to attain a given net helicity increases with decreasing concentration. The monomeric regime, where the curves become vertical again (indicating concentration independence), is uninteresting, for in this regime we cannot speak of a polymerized state.²⁷ It follows from Fig. 1 that in experiment the values of certain parameters cannot be obtained from the chirality amplification in all three regimes. In the long-chain regime, for instance, one cannot determine $\langle N \rangle$ from the measured net helicity, whereas the shorter the chains become (regimes II and III), the more difficult it becomes to fix σ . It is therefore necessary to obtain results for the relationship between $\langle \eta \rangle$ and x in at least two regimes to determine both parameters or to fix $\langle N \rangle$ in an independent experiment (e.g., in a light-scattering experiment).

The impact of the degree of cooperativity (which is a function of the free-energy cost of a helix reversal) on the strength of the chirality amplification is shown in Fig. 1(b). Here we have indicated the fraction of chiral material needed to induce a net helicity of half its maximum value, defined as x_* , for values of σ ranging from 10^{-8} to 1 . [For reasons of clarity, we now plot $\phi \exp(E)$ on the vertical axis, rather than $\xi_0^{-2} \phi \exp(E)$.] Our results confirm that the chirality amplification does indeed increase with increasing cooperativity—i.e., that x_* decreases with decreasing values of σ . It is also obvious, however, that the effects of mass action and cooperativity are not independent: in the monomeric regime (III) the value of σ does not influence the strength of the sergeants-and-soldiers effect (since the chains will be on average too short to allow for a helix reversal) and all curves coincide, whereas in the long-chain regime (I) the effect of σ is strongest. We further notice that for sufficiently low values of σ , all curves lie quite close together when plotted on a linear scale. This implies that an increase in the cooperativity in this regime may not lead to a noticeable change in the amount of chiral material needed to obtain a fixed net helicity, except when placed on a logarithmic scale.

It may seem surprising that even in the absence of any cooperativity or chirality amplification with $\sigma = 1$, a fraction of chiral monomers of x that equals one-half does not always lead to a mean net helicity $\langle \eta \rangle$ of one-half. Figure 1(b) shows that in fact more chiral material is necessary to get this fixed net helicity when the overall concentration (and thus the mean size) decreases. This is a consequence of our assumption that a bond is only influenced by a chiral monomer if it follows this monomer. The shorter the aggregates, the larger the probability that a chiral monomer turns out to be the last molecule of the chain and, as such, does not change the conformation of any bond.

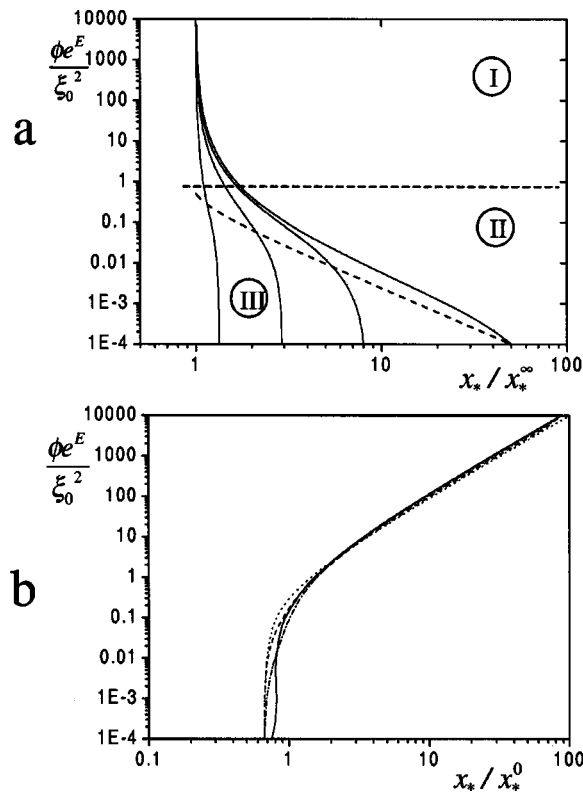


FIG. 2. (a) $\xi_0^{-2} \phi \exp E$ vs x_*/x_*^∞ , for different values of the cooperativity parameter σ . From left to right: $\sigma=1$, $\sigma=0.1$, $\sigma=10^{-2}$, and $\sigma=10^{-4}$. The Roman numbers and dashed lines indicate the regimes, as in Fig. 1(a). (b) $\xi_0^{-2} \phi \exp E$ as a function of x_*/x_*^0 , for different values of the cooperativity parameter σ . Solid line: $\sigma=10^{-4}$. Dot-dashed line: $\sigma=10^{-2}$. Dashed line: $\sigma=0.1$. Dotted line: $\sigma=1$. Lines indicating the regimes are omitted for clarity.

In the long-chain limit $\phi \exp(E) \rightarrow \infty$, x_* approaches a universal value x_*^∞ that depends only on σ (Ref. 14):

$$x_*^\infty = \frac{3\sigma + 3\sqrt{3\sigma + \sigma^2}}{6 + 4\sigma + 4\sqrt{3\sigma + \sigma^2}}. \quad (17)$$

It makes sense, then, to rescale $x_* \rightarrow x_*/x_*^\infty$. This produces a universal curve for conditions in the long-chain regime, as shown in Fig. 2(a). The figure again demonstrates the influence of finite-size effects, which is to reduce the degree of chirality amplification.

In a similar vein we can produce a universal curve for the short-chain regime by noting that, in this regime, the size of the aggregates lies between unity and, say, a bare correlation length. In that case a single chiral monomer is sufficient to change the conformation of an entire aggregate of size $\langle N \rangle \approx \langle N \rangle_0$, implying that only very few chiral monomers are needed to induce a large net helicity if $\langle N \rangle \gg 1$. As a consequence, the probability of finding two chiral monomers in a single aggregate approaches zero if x is not very much larger than x_* . The number of aggregates (per unit volume) whose conformation is changed by the presence of a chiral agent must be approximately equal to the number of chiral monomers $x\phi$. The net helicity per unit volume is then given by the number of such aggregates divided by the total number of aggregates, $\phi \langle N \rangle_0^{-1}$, and equals $x \langle N \rangle_0$. We therefore rescale $x_* \rightarrow x_*/x_*^0$, with $x_*^0 = \langle N \rangle_0^{-1}$.

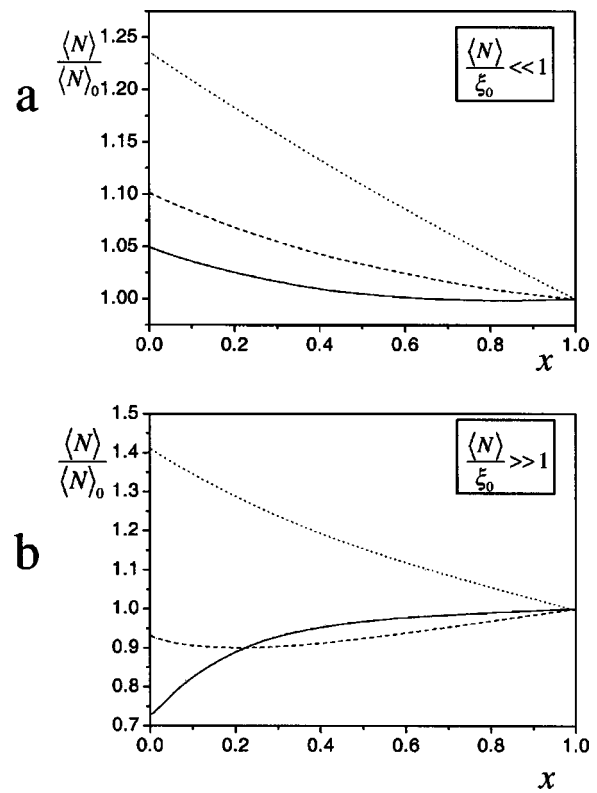


FIG. 3. (a) Relative mean aggregate size $\langle N \rangle / \langle N \rangle_0$ vs the fraction of chiral material x in the short-chain limit with $\phi \exp E=1$, for $\sigma=10^{-3}$ (solid line), $\sigma=0.1$ (dashed line), and $\sigma=1$ (dotted line). (b) As (a), for the long-chain limit, with $\phi \exp E=10^6$.

As can be seen in Fig. 2(b), the rescaling produces a set of curves that nearly overlap for all concentrations, not just in the short-chain regime. In the long-chain regime universal scaling can be observed, since x_*/x_*^∞ scales as $x_*^\infty \langle N \rangle_0$ while $\xi_0^{-2} \phi \exp E$ scales as $\xi_0^{-2} \langle N \rangle_0^2$ and both x_*^∞ and ξ_0 are functions of σ only. On the other hand, in the monomer regime, the overlap of the curves occurs because $\langle N \rangle_0$ approaches the value unity, and $x_*/x_*^0 = x_* \langle N \rangle_0 \rightarrow x_*$ for all σ . Small deviations from the universal curve arise because we use $\langle N \rangle_0$ rather than $\langle N \rangle$ to rescale the curves.

In contrast to the “bare” aggregate size $\langle N \rangle_0$, the actual mean size $\langle N \rangle$ depends not only on the overall concentration of aggregating molecules and the strength of the physical bonds, but also on the composition of the aggregates, albeit only weakly so. The reason for this dependence is that the chiral content influences the number of helix reversals in an aggregate and the aggregate may respond to the presence of helix reversals by changing its size. The influence of the composition on the mean size of the aggregates is shown in Fig. 3 for the limits of small [Fig. 3(a)] and large [Fig. 3(b)] degrees of polymerization. We have plotted here $\langle N \rangle / \langle N \rangle_0$ against x for different values of σ (being 10^{-3} , 0.1 , and 1), and we find that the composition influences the mean aggregate size by no more than a factor 2 in either limit.

V. COMPARISON TO EXPERIMENT

We now compare the results of our theory with circular-dichroism measurements by Brunsveld and co-workers on

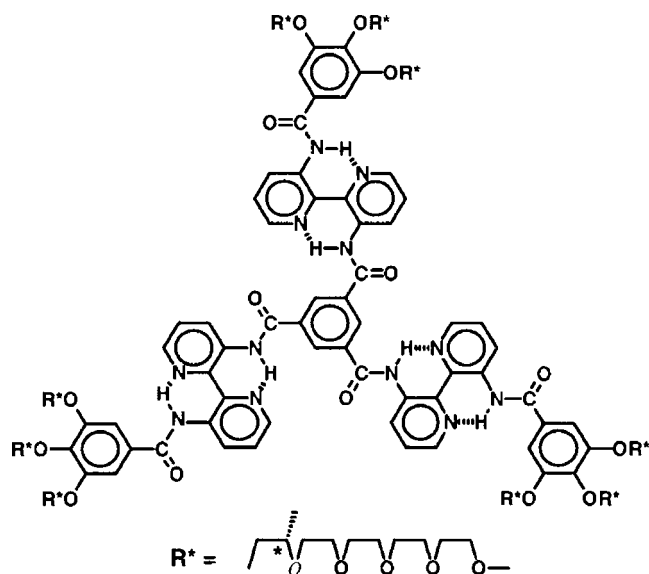


FIG. 4. Chemical structure of the discotic molecule of Brunsveld *et al.* (Ref. 9). Shown is the chiral monomer; the achiral monomer lacks the methyl side groups in the solubilizing chains.

mixtures of chiral and achiral discotic molecules dissolved in *n*-butanol and water at overall concentrations of 10^{-4} and 10^{-5} mol/l (Refs. 8 and 9). The molecules in question have a large apolar core, surrounded by nine flexible, polar sidechains. The chiral monomer has a stereocenter in each of these sidechains (see Fig. 4). In both solvents a strong chirality amplification is found, especially so in *n*-butanol, where less than 1% of chiral material is needed to induce a net helicity of half its maximum value measured. Again, this level of cooperativity is a remarkable finding in self-assembled polymers, which are after all bound with fairly weak bounds. Interestingly, the net helicity in *n*-butanol is concentration dependent, whereas for the solution in water the curves for the two concentrations overlap. It appears that in the former solvent, the chirality amplification conforms to regime II, while in the latter it conforms to regime I. By fitting the theory to experiment, we obtain values for our model parameters, allowing us to compare them for different conditions. Although we cannot *predict* values for the phenomenological parameters from the molecular architecture and solvent structure, the values found from a fit of the experiments with our model do give an indication as to what aspects of the molecular architecture and solvent composition are of importance.

It is important to stress at this point that if one measures the optical activity of a solution, one does not specifically measure the net helicity, but rather the chiral content of the sample,¹⁴ at least in principle. However, in the case of the experiments of Refs. 8 and 9 it is not necessary to include a contribution from the free monomers. The reason is that in the discotic molecules studied in Refs. 8 and 9 the chromophore and chiral group are separated to such an extent that no Cotton effect is measured for a solution containing the homochiral monomers in a molecularly dispersed state. Therefore, circular dichroism only measures the *supramolecular chirality* (or the helicity) in this particular system.

However, this does not mean that the measured Cotton effect is identical to the net helicity per bond as defined in Eq. (12). In fact, the strength of the Cotton effect measured in experiment is determined by the total amount of optically active material in a probe volume as well as by the optical properties of the two types (homochiral and achiral) of molecules. The former depends, e.g., on the concentration of dissolved material and on the optical path length. To account for this, we introduce a constant of proportionality α that links the theoretical net helicity per bond and the measured optical effect. For both sets of experiments, we have normalized the data of Brunsveld *et al.*^{8,9} to give a value of unity at the maximum in the curves, implying that we presume that full saturation of the Cotton effect does take place.

To properly deal with the optical properties of the molecules, one needs to realize that the measured effect may depend on the type of monomer and the type of bond it is involved in. Thus we introduce a relative strength γ that distinguishes between contributions for a bond following a chiral monomer and one following an achiral monomer in an assembly, and assign this weighing factor to every bond that follows a chiral monomer, the fraction of which is $z(z+1)^{-1}$. We assign the weight 1 to bonds that follow an achiral monomer, the fraction of which equals $(z+1)^{-1}$. The mean net helicity obtained from experiment we denote by $\langle \eta \rangle'$, and it is plausibly given by a linear superposition of the two contributions mentioned. Hence,

$$\langle \eta \rangle' = \alpha \langle \eta \rangle \left[1 + (\gamma - 1) \frac{z}{z+1} \right], \quad (18)$$

where γ and α are now treated as additional fitting parameters. It follows from Eq. (18) that if γ is smaller than unity (achiral monomers have a larger contribution to the net helicity than chiral ones), $\langle \eta \rangle'$ becomes a nonmonotonic function of x . This is not so for $\gamma \geq 1$, in which case $\langle \eta \rangle'$ remains monotonic in x .

We first discuss the experiment that displays a concentration dependence, in which the solvent is *n*-butanol, and after that we compare our theory to the experimental results from the aqueous solutions. Since the chirality amplification is concentration dependent in the solvent *n*-butanol, we must reside within the short-chain regime, where $1 \ll \langle N \rangle \ll \xi_0$; it follows that $\sigma \approx \xi_0^{-2} \ll 1$. We have shown in Fig. 1(b) that for these values of σ , the net helicity is insensitive to the value of σ . Therefore, the value of σ becomes arbitrary and we set $\sigma = 10^{-8}$. We now perform a fit at a single value of x —namely, x_* —to find the proper value of $\phi \exp(E)$. For the concentration of 10^{-4} mol this turns out to be at $\phi \exp(E) = 6 \times 10^4$ —i.e., $\langle N \rangle \approx \langle N \rangle_0 \approx 250$.

We now plausibly assume that the bond energy $-E$ does not change with concentration. Then, if our assumption that $\langle N \rangle \ll \xi_0$ is valid, we should obtain good agreement with the measurements at 10^{-5} mol if we use $\phi \exp(E) = 6 \times 10^3$ (a factor of 10 lower). Indeed, this turns out to be the case, indicating that our simple theory takes the concentration dependence into account in a proper way (see Fig. 4). We can determine the reference free energy from the values of $\phi \exp(E)$ since ϕ is known.²⁸ This gives $-E = -19(k_B T)$, which is close to the values of $-15(k_B T)$ and $-16(k_B T)$,

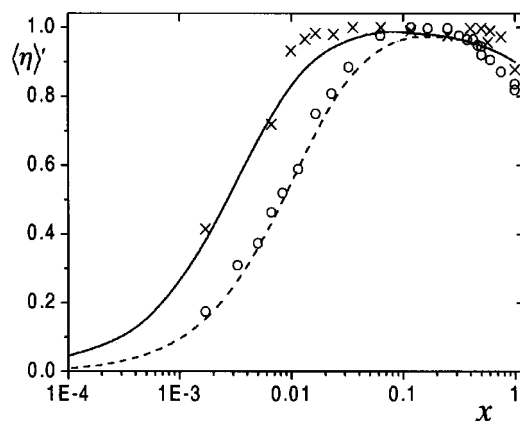


FIG. 5. Fit of the theoretical net helicity $\langle \eta \rangle'$ versus x to experimental data of Brunsveld *et al.* (Ref. 8) in *n*-butanol at two concentrations. (Circles: 10^{-5} mol. Crosses: 10^{-4} mol.) Dashed line: curve fit for 10^{-5} mol with fitting parameters $\phi \exp E = 6 \times 10^3$, $\sigma = 10^{-8}$, $\alpha = 1$, and $\gamma = 0.9$. Solid line: curve fit for 10^{-4} mol with fitting parameters $\phi \exp E = 6 \times 10^4$, $\sigma = 10^{-8}$, $\alpha = 1$, and $\gamma = 0.9$.

obtained from measurements at similar concentrations of *homochiral* discotic molecules in the solvent *n*-butanol.^{8,18}

If we choose the values of $\phi \exp(E)$ mentioned above, we get good agreement over the entire range of fractions of chiral material, with the exception of the high- x regime, where a maximum is observed experimentally. As implied earlier, the presence of a maximum indicates that bonds following achiral molecules have a larger contribution to the helicity than do those following chiral ones and thus that the ratio between the contributions to the net helicity of chiral and achiral monomers γ must be smaller than unity.¹⁴ We perform a curve fit on the maximum in the curve and obtain good agreement for $\gamma = 0.9$ and $\alpha = 1$ for both concentrations (see Fig. 5).

We now compare our theory to circular-dichroism measurements on mixtures of the same chiral and achiral discotic molecules in water, for which the chirality amplification is concentration independent for the concentrations studied.⁹ This indicates that $\langle N \rangle \gg \xi_0$ and, thus, that the chirality amplification is an invariant of $\phi \exp(E)$ (see Fig. 1). It turns out that the current theory reproduces our earlier fit¹⁴ almost exactly (see Fig. 6 and inset) if we use the same fitting procedure as before (fixing $\sigma = 6.4 \times 10^{-3}$ at the point x_* and $\gamma = 0.65$ and $\alpha = 1.15$ from the maximum in the curve) (Ref. 29) and set $\phi \exp(E)$ for both concentrations to be large (but obviously a factor 10 apart: we set $\phi \exp(E) = 10^7$ for 10^{-4} mol and 10^6 for 10^{-5} mol). This shows that the earlier approximate theory is indeed a special case of the current one and is recovered in the infinite-chain limit, as it should be.

As discussed, our choice of $\phi \exp(E)$ here is arbitrary. As long as we choose a value that corresponds to the long-chain limit, we will obtain the proper concentration independence of the Cotton effect. Therefore, we cannot fix E from the circular-dichroism measurements. However, we are able to estimate a minimum value for this quantity if we determine the value of $\phi \exp E$ for which the chirality amplification becomes discernably concentration dependent,³⁰ for the given value of $\sigma = 6.4 \times 10^{-3}$. For this particular system the

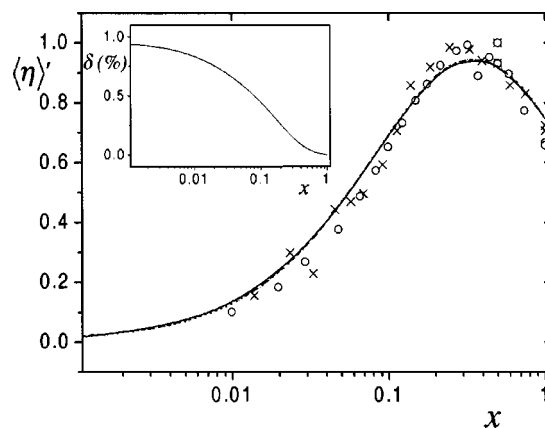


FIG. 6. Fit of the theoretical mean net helicity $\langle \eta \rangle'$ versus x to experimental data of Brunsveld *et al.* (Ref. 9) in water at two concentrations. (Circles: 10^{-5} mol. Crosses: 10^{-4} mol.) All three lines have the fit parameters $\sigma = 0.0064$, $\alpha = 1.15$, and $\gamma = 0.65$. Dashed line: curve fit for $\phi \exp E = 10^7$. Solid line: curve fit for $\phi \exp E = 10^6$. Dotted line: curve fit with the earlier model, valid in the long-chain limit (Ref. 14). Inset: the relative difference between the mean net helicity in the current model for $\phi \exp E = 10^6$ and that in the earlier model, in percent.

transition between concentration dependence and independence occurs at $E = 18$, from which follows that E must be smaller than this value for a concentration dependence to occur for these molecules in water (with this σ) at these concentrations.²⁸ Alternatively, one might decrease ϕ and thus enter the concentration-dependent regime.

VI. CONCLUSIONS

The one-dimensional, two-component Ising model, coupled to the theory of linear self-assembly as outlined in this paper, provides a good description of the concentration dependence of the sergeants-and-soldiers effect in helical supramolecular polymers. This shows that our idealized model captures the physics of the problem. We describe the properties of the system with a number of phenomenological free-energy parameters and find that an increase of the penalty of a helix reversal leads to a larger chirality amplification in the long-chain limit and that an increase of the solute concentration leads to an increase in the chirality amplification in the short-chain limit. However, we also find that, in the former limit, the strength of the sergeants-and-soldiers effect becomes insensitive to changes in the concentration, just as it becomes insensitive to the value of the free energy of a helix reversal in the latter limit. As a result, it may be difficult to determine the mean aggregate size from circular-dichroism experiments at high concentrations and it may be equally difficult to determine the free energy of a helix reversal from measurements at low concentrations. The dependence of the chirality amplification on the (mean) chain length and the central role played by the cooperativity mirror conclusions of earlier work on conventional copolymers.³ The theory we present shows quantitative agreement with circular-dichroism measurements of mixtures of chiral and achiral discotic molecules in the solvents water and *n*-butanol, for two concentrations that differ by a factor of 10 (Refs. 8 and 9). When we assume that chiral monomers have a lower

contribution to the measured helicity than do achiral ones, we can reproduce the experimentally measured maximum in the Cotton effect as a function of the fraction chiral material. For long enough chains, the agreement between experiment and theory is identical to that obtained with our earlier, approximate treatment.¹⁴ In this regime, it is perhaps more convenient to use the earlier, less cumbersome, treatment.

ACKNOWLEDGMENTS

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- ²⁶Strictly speaking, the mean net helicity should contain an averaging over the $(N-1)$ bonds, rather than over the N monomers. However, this would require changing the definition of ϕ in this context, and it turns out that the effect of this improvement is negligible.
- ²⁷As a result of our definition of $\langle \eta \rangle$, Eq. (12), which does not include free monomers, we get nonzero values for $\langle \eta \rangle$ even if almost all the material is present in monomeric form.
- ²⁸To calculate the volume fraction from the molar concentration, a density for the discotic molecule of 1.3 g mL^{-1} was used. We obtained this number from x-ray measurements in the solid state. The molecular weight of the discotic lies around 3400 g mol^{-1} . We have neglected the difference in molar mass between the chiral and achiral molecules.
- ²⁹Note that the value of $\alpha > 1$, necessary to obtain good agreement between theory and experiment, could indicate that the state of full one-handed helicity ($\langle \eta \rangle' = 1$) was not reached in experiment. Indeed, contrary to Fig. 5, Fig. 6 does not display a clear "plateau" of maximum helicity, but rather a sharp peak.
- ³⁰We arbitrarily quantify the transition between concentration dependence and independence to take place where a change in concentration of a factor of 10 induces a shift of 10% in the mean net helicity near the point where $\langle \eta \rangle = 1/2$.