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Isotropic and nematic liquid crystalline phases of adaptive rotaxanes

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We describe the thermodynamics of a solution of rotaxanes which can change their length from a short state of length L to a long state of length qL in response to their surrounding environment. We call these rotaxanes “adaptive.” We show that such a system can exhibit both isotropic and nematic liquid crystalline phases. The system shows several interesting kinds of behaviour. First we predict that the fraction of short-length rotaxanes increases linearly with concentration and is a maximum at the critical concentration that marks the isotropic to nematic transition. Second, the critical concentration shows a minimum at a certain value of q . Our model suggests that the effect of adaptive length changes is most dramatic at small q and where the long state is slightly favoured. © 2016 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4943098>]

I. INTRODUCTION

A rotaxane is a wheel and axle molecule, where a molecular ring or rings are threaded onto an axle. This is then stoppered at both ends so the rings cannot escape. Their synthesis is an active area of research^{1–15} and the production of these mechanically linked molecules opens up many new possibilities for phenomena on the molecular scale. Some rotaxanes act as two-state switches. They can do this because they have 2 stations along the axle, and the rings attach preferentially to these stations. The switching between stations can be controlled by external influences such as solvent pH, ion interaction, redox reaction, solvent quality, or light. Another way of moving the ring is to attach a rigid rod to it and then compressing it with an AFM tip. This was done by Brough *et al.*² Later Sevick and Williams¹⁶ showed how such a system, with many rings, could behave as a molecular shock absorber.¹⁷ Switching changes the length of this piston-rotaxane molecule. In Figure 1 we depict such a switchable rotaxane where there is a short state and a long state, the ratio of the lengths of these states being q . This suggests that switching rotaxane molecules between states might create interesting, controllable liquid crystalline phases.

Liquid crystals¹⁸ are solutions of anisotropic molecules which have no long-range positional order, like a liquid, but can have phases which possess different degrees of molecular orientation similar to crystalline ordering. The phases in lyotropic liquid crystals are determined by the concentration of the molecules, $c = N/V$ (N the number of solute particles in a volume V) which can be altered by addition of solvent, Figure 2. In dilute solutions, the fixed-sized anisotropic molecules have no long-range translational or orientation order—the solution is isotropic. However, with an increased concentration, a nematic phase appears where the molecules still have no translational order, but self-align to have

directional order along their long axis. This orientationally ordered nematic phase is birefringent, optically detectable using cross polarised filters, and is the principle concept behind liquid crystalline displays. The fundamental theory for these systems was produced by Onsager in 1949.^{19–21} Recently this work was extended to a two-state rotaxane system, where an *external* influence,²² controlled by the experimenter, could switch the rod length from short to long. This enables a sudden transition from isotropic to nematic, without changing the concentration of rods.

In this paper, we describe a somewhat different rotaxane system. The rotaxane can exist in two different states, one of length L and the other of length qL , but the molecule itself decides which state to be in on the basis of the what minimises the total free energy of the system. We call such rotaxanes “adaptive.” This is in marked contrast to the recent work of He *et al.*,²² where the rotaxanes are forced to be in one state or the other by external control of the system, as for example, by changing the pH.

As a simple example, consider a dilute solution of adaptive rotaxanes between two plates a distance H apart. The rotaxanes can choose to have lengths L or qL , with $q > 1$. If the distance between plates is larger than the largest molecular dimension $H > qL$, we would find 1/2 of the molecules of length L and the other half of length qL . However, as H gets smaller, there will be a gradual bias towards shorter rods because the longer rods can only fit by re-orientating parallel to the plates. The rotaxanes “adapt” to their external environment.

In the case considered in this paper, the rotaxanes adapt, not because of an imposed confinement by plates, but because of hard-body interactions with surrounding rods. The remainder of the paper is organised in the following way. In Sec. II, we review Onsager’s classical treatment of lyotropic liquid crystals formed from homogeneous, fixed-length rods. In Sec. III, we extend this theory to an adaptive 2-state rotaxane and present results in the following section. In particular, we show how the critical concentrations for the transitions, the order parameters, and the fraction of rotaxanes in the short

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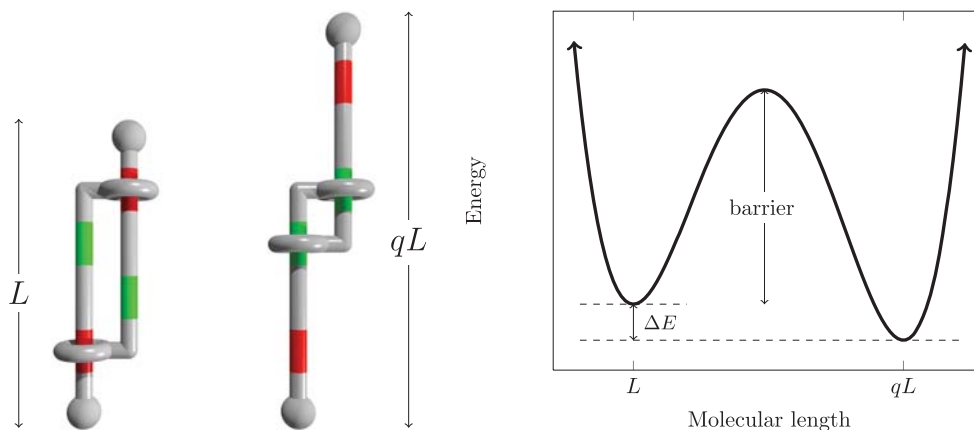


FIG. 1. Illustration of a 2-state rotaxane in short and long states and the energy of an isolated rotaxane switch as a function of molecular length, showing the short and long states as minimal energy states. Attractive stations along the axles are depicted as green and red regions. When the rings reside within the attractive red stations (left), the rotaxane is in its short state, characterised by the molecular length, L . When the rings reside within the attractive green stations (middle), the rotaxane is in its long state, characterised by the molecular length qL . The ratio of long to short state lengths, q , is set by the synthetic design of the molecule. In adaptive rotaxanes, the energy difference between states, ΔE , is small, on the order of $k_B T$. If the long state has lower energy, it is favoured at vanishingly small concentrations; but because ΔE is small, the short state may be favoured at high solution concentrations so as to lower the free energy of the solution. If $|\Delta E| \gg k_B T$, the rotaxane will not be adaptive and solutions of rotaxanes will behave like solutions of fixed-length rods. For the adaptive rotaxanes considered here, the energy barrier between the states is assumed to be large so that the individual rotaxane states (short or long) are the only allowed states. Here we consider the equilibrium liquid crystalline phases of a solution of this adaptive two-state rotaxane.

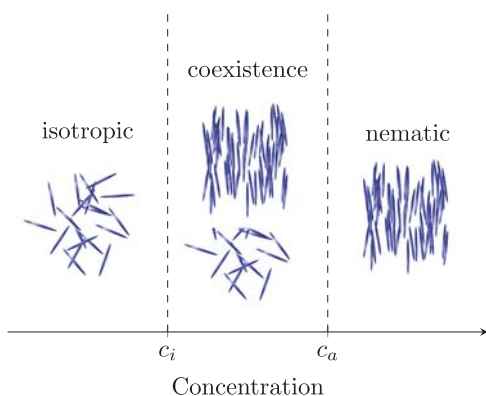


FIG. 2. Illustration of lyotropic liquid crystalline phases for a solution of fixed-length rods of one size and with simple hard-body interactions. The volume-excluding rods are isotropic for concentrations up to c_i , above which appears a coexisting nematic phase. As concentration increases from c_i to c_a , the volume of nematic phase increases at the expense of the isotropic phase, until at c_a , the solution is entirely in the nematic phase. Onsager predicted the critical concentrations of rods of length, L and diameter d to be $c_i = 3.34(\frac{\pi}{4}L^2d)$ and $c_a = 4.49(\frac{\pi}{4}L^2d)$.

state, depend on the synthetic design parameter q and energy bias between the two adaptive states. The behaviour we encounter is sometimes unexpected, and although we can give *post-hoc* explanations of all of it, it would be very difficult to predict it without the model and its numerical predictions.

This work should be seen in the context of other works on adaptive systems. In particular, wormlike micelles,²³ radially compressible rods,²⁴ and crowding of proteins.²⁵

II. FIXED-LENGTH RODS

We start with a brief review of the classical Onsager theory¹⁹ for monodisperse rods of length L , diameter d , and concentration $c = N/V$, where N is the number of rods in a volume V . The physics is essentially as follows. Onsager

assumes that the only forces between the rods are those of hard bodies, i.e., the interaction is zero except in cases of attempted overlap, and all overlaps are forbidden. In such a system, the free energy is entirely entropic, and the system minimises the free energy by maximising the entropy. The entropy is k_B multiplied by the logarithm of the number of configurations, so that all we need to do is count the configurations. The entropy is of two kinds, translational and rotational. First there is the translational entropy of the centres of each molecule. This is maximised by having the rods placed randomly within the container. The second kind is the orientational entropy, which is maximised by the rods pointing in every direction with equal probability. At infinitely small concentrations, $c \rightarrow 0$, the rods do not interact and both the translational and orientational entropy are maximised by having the rods uniformly distributed in space and in direction. However, as c is increased towards the characteristic concentration $\sim 1/(L^2d)$, the rods begin to interact and we find overlap. At these low concentrations, the orientation is still totally random, but certain positions of the centre of mass of two rods are forbidden. These forbidden positions lead to a decrease in the translational entropy. The system can avoid some of these forbidden positions by aligning the rods so that they preferentially point along a particular direction. This decreases the orientational entropy, but increases the translational entropy.

The free energy per rod (see [Appendices A and B](#)) of a homogeneous solution of N rods of length L and diameter d in a volume V is

$$\frac{F[\Psi]}{Nk_B T} = \ln \frac{N}{V} - 1 + \int d\mathbf{u} \Psi(\mathbf{u}) \ln [\Psi(\mathbf{u})] + \frac{1}{2} \frac{N}{V} \int \int d\mathbf{u} d\mathbf{u}' \Psi(\mathbf{u}) \Psi(\mathbf{u}') 2L^2 d |\mathbf{u} \times \mathbf{u}'|. \quad (1)$$

Here $\Psi(\mathbf{u})$ is the orientational distribution function for the rods and \mathbf{u} is a unit vector specifying the rod direction. The term $\ln(N/V) - 1$ is the translational entropy, assuming

a homogenous distribution. The term in $\ln(\Psi)$ is the orientational entropy, and the final term accounts for the rod-rod interactions. In essence, this final term is the reduction in translational entropy caused by rod-rod interactions.

The equilibrium orientation distribution is determined by the condition that the free energy is minimal for all variations of $\Psi(\mathbf{u})$, subject to the mathematical condition that the distribution is normalised. This results in a non-linear equation for $\Psi(\mathbf{u})$ which cannot be solved analytically. There is then a choice of solution methods. One approach is brute-force numerical minimisation. Onsager¹⁹ chose a more elegant trial function approach, using the function (Figure 3),

$$\Psi(\mathbf{u}) = \frac{\alpha}{4\pi \sinh \alpha} \cosh[\alpha \mathbf{u} \cdot \mathbf{n}], \quad (2)$$

where \mathbf{n} is an arbitrary unit vector (the director) and α is a parameter representing the degree of alignment, to be determined analytically from minimisation of the free energy. $\alpha = 0$ corresponds to an isotropic state where rods adopt all angles with equal likelihood or equivalently, $\Psi(\mathbf{u}) = (4\pi)^{-1}$, and $\alpha = \infty$ corresponds to a perfectly aligned collection of rods, Figure 3. This trial function method replaces a function with an infinite number of variables $\Psi(\mathbf{u})$ with a single variable α to be minimised over. It thus introduces some approximation, but is in keeping with the other approximations in the theory.

The parameter α is closely related to the order parameter, S , which also measures the degree of alignment. S is defined by $S \equiv \langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \rangle$, where θ is the angle between the rod and the nematic director, \mathbf{n} . For the isotropic state, $S = 0$ and any non-zero S implies a nematic phase. In the limit of perfect alignment, $S \rightarrow 1$. We can easily express S in terms of α via

$$S = 1 + 3\alpha^{-2} - 3\alpha^{-1} \coth \alpha \quad (3)$$

so that for small α , $S \approx \alpha^2/15$, while for large α , $S \approx 1 - 3\alpha^{-1}$.

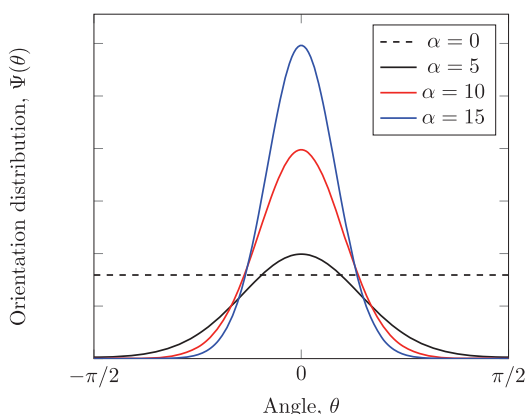


FIG. 3. Onsager's trial function, $\Psi(\theta)$, versus angle, θ for several different parameters, $\alpha \cdot \theta = \cos^{-1}(\mathbf{u} \cdot \mathbf{n})$ is the angle that the rod makes with an arbitrary vector, \mathbf{n} , the director. The parameter α characterises the degree of alignment, with $\alpha = 0$ describing the isotropic state with no orientational order, where $\Psi(\theta) = (4\pi)^{-1}$. In our extension to adaptive rotaxanes, we use this same trial function to describe the orientational ordering of rotaxanes in nematic phases. As rotaxanes in the short and long state will be orientationally ordered to different degrees, we introduce the orientation distribution Ψ_S , with parameter α_S to describe the orientational ordering of rotaxanes in the short state, and Ψ_L and α_L for rotaxanes in the long state.

At low concentration, the free energy is minimised when $\alpha = 0$; this corresponds to a single isotropic phase. At high concentration, the free energy is minimised when α takes on a larger value corresponding to a single nematic phase. However between two critical concentrations c_i and c_a , there are two coexisting phases, one isotropic at concentration $c = c_i$ and the other nematic at concentration $c = c_a$. In each of these phases, the value of α is different. The first phase corresponds to an isotropic phase of N_i rods and volume V_i . The free energy per rod in this isotropic phase is $F_i = F(N_i, V_i, \alpha_i = 0)$, where F is of the form given by Eq. (1). The second phase corresponds to a nematic phase of N_a rods in volume V_a with orientation α_a . The free energy per rod of the nematic phase is $F_a = F(N_a, V_a, \alpha_a)$. The number of rods in each phase and the relative volume of the phases vary within the concentration range $c_i \leq c < c_a$, where c is the concentration of the entire solution i.e., $c = (N_i + N_a)/(V_i + V_a)$. These are determined by writing the free energy as a sum of the free energy of the isotropic and nematic phases,

$$F = F_i(N_i, V_i, \alpha_i = 0) + F_a(N_a, V_a, \alpha_a) \quad (4)$$

and minimising F with respect to N_i, V_i subject to the constraints of constant total volume and number of molecules, $V = V_i + V_a$ and $N = N_i + N_a$. Equivalently, we can determine the phase compositions and volumes by equating the chemical potential of the molecules in each coexisting phase

$$\frac{\partial F_i}{\partial N_i} = \frac{\partial F_a}{\partial N_a}, \quad (5)$$

and by equating the osmotic pressure in each phase, or

$$\frac{\partial F_i}{\partial V_i} = \frac{\partial F_a}{\partial V_a}. \quad (6)$$

These two thermodynamic relations coupled with the constraints of constant total number of molecules and constant total volume fully specify the concentrations and the relative fraction of coexisting isotropic and nematic phases. In practice, if we know c_i and c_a and we put N rods in a solution of volume V , we can calculate the number of rods in each coexisting phase and the volume of these phases using the fact that $V_i c_i + V_a c_a = N$ and $V_i + V_a = V$. To summarise the results for a solution of homogenous hard rods, we have the following:

1. $0 < c < c_i$ the solution is isotropic,
2. $c_i < c < c_a$ an isotropic phase of density c_i coexists with a nematic phase of density c_a ,
3. $c_a < c$ the solution is nematic.

In Onsager's solution for homogeneous rods of fixed length L and diameter d , the critical concentrations are $c_i = 3.34(\frac{\pi}{4}L^2d)^{-1}$ and $c_a = 4.49(\frac{\pi}{4}L^2d)^{-1}$. Both these concentrations contain the characteristic concentration $\sim L^2d$, which is essentially the inverse excluded volume of one rod.

III. 2-STATE ADAPTIVE ROTAXANES

Before we consider the free energy of the adaptive system, we first need to determine how many coexisting phases there can be in this system. In the case of rods of fixed length, the Gibbs phase rule gives that the number of coexisting phases

can be at most 2. In the system where we have rods of two possible lengths, this is also true, for the reason that we only have one species of rod, which can take two possible lengths, i.e., the rod lengths are always in equilibrium with each other. This in fact makes it less complicated than a system consisting of rods of two different fixed lengths.^{26,27} We thus expect coexistence of only two phases, one isotropic and one nematic, just as in Onsager's fixed length rod problem. However, the critical concentrations for the transitions c_i and c_a will of course be different.

To describe the liquid crystalline phase diagram of 2-state adaptive rotaxanes, we extend Onsager's treatment to a solution of N molecules of fixed diameter d , a fraction x in the short state, having length L and a fraction $(1-x)$ in the long state with length qL . Molecules of different length may orient differently: in a dilute solution, the molecules will be randomly oriented irrespective of their length; however at higher concentrations molecules in the long state will be oriented more strongly than those in the short state. Consequently, we introduce two orientation distribution functions, $\Psi_S(\mathbf{u})$ representing molecules in the short state and $\Psi_L(\mathbf{u})$ in the long state. Moreover, there can be an intrinsic energy difference between short and long states (Figure 1) which will provide a bias or preference for one of the states: we let ΔE represent the energy of a rotaxane in the long state relative to the short state, $\Delta E = E_L - E_S$. We emphasise that this intrinsic bias is independent of the local environment of the molecule, so that in any case where $\Delta E \neq 0$, there will be differing populations of short and long states for an isolated rotaxane.

The free energy derivation is similar to that for the fixed-length system (see Appendices A and B), with the exception that, because of two possible states of each molecule, we have two orientational distribution functions and the partition function is augmented by a factor $Z_2[x]$,

$$Z[\Psi_S, \Psi_L, x] = Z_0[\Psi_S, \Psi_L, x] Z_1[\Psi_S, \Psi_L, x] Z_2[x].$$

$Z_2[x]$ corresponds to the number of ways that N non-interacting rotaxanes partition between the short and long states

$$Z_2[x] = \frac{N!}{(xN)!((1-x)N)!} \exp\left[\frac{xN\Delta E}{k_B T}\right],$$

where x is the fraction of short states. The contribution to the free energy associated with molecular switching is $F_2[x] = -k_B T \ln Z_2[x]$, or

$$\frac{F_2[x]}{Nk_B T} = x \ln x + (1-x) \ln(1-x) - x \frac{\Delta E}{k_B T}. \quad (7)$$

The first two terms of the RHS are recognisable as the entropy of mixing. Here they represent a configurational entropy. Any deviation from equal numbers of long and short is penalised. In the absence of any interactions between the rods, and assuming that there is no bias ($\Delta E = 0$), the minimum lies at $x = 1/2$. With an inbuilt bias but no interactions, we find the minimum is at $x = \frac{1}{2} \exp[-\frac{\Delta E}{k_B T}]$. The contribution to the free energy by distributing these non-interacting rotaxanes with orientational distribution functions Ψ_S and Ψ_L is $F_0[\Psi_S, \Psi_L, x] = -k_B T \ln [Z_0[\Psi_S, \Psi_L, x]]$, and is, following Sec. II,

$$\begin{aligned} \frac{F_0[\Psi_S, \Psi_L, x]}{Nk_B T} &= \ln [N/V] - 1 + x \int d\mathbf{u} \Psi_S(\mathbf{u}) \ln [\Psi_S(\mathbf{u})] \\ &+ (1-x) \int d\mathbf{u} \Psi_L(\mathbf{u}) \ln [\Psi_L(\mathbf{u})]. \end{aligned} \quad (8)$$

Finally, the contribution to the free energy from the interactions between rotaxanes requires the excluded volume between the 3 possible pairs (short-short, short-long, long-long). The excluded volume of a pair of molecules, β , depends upon the molecular length, which can take on values of L , in the short state, or qL in the long state. The 3 possible values of β are

$$\begin{aligned} \beta_{L,L}(\mathbf{u}, \mathbf{u}') &= 2L^2 d |\mathbf{u} \times \mathbf{u}'|, \\ \beta_{S,L}(\mathbf{u}, \mathbf{u}') &= 2qL^2 d |\mathbf{u} \times \mathbf{u}'|, \\ \beta_{S,S}(\mathbf{u}, \mathbf{u}') &= 2q^2 L^2 d |\mathbf{u} \times \mathbf{u}'|. \end{aligned} \quad (9)$$

Amongst the $N^2/2$ pairwise interactions, x^2 is the mean fraction of the pairwise interaction that is between molecules in the short state, $(1-x)^2$ is the mean fraction of pairs in the long state, and $2x(1-x)$ is the mean fraction of pairwise interactions involving molecules in different length states. Thus, the contribution to the free energy due to pairwise interactions is

$$\begin{aligned} \frac{F_1[\Psi_S, \Psi_L, x]}{Nk_B T} &= \frac{N}{2V} \left[(1-x)^2 \int \int d\mathbf{u} d\mathbf{u}' \beta_{L,L} \Psi_L(\mathbf{u}) \Psi_L(\mathbf{u}') \right. \\ &+ 2x(1-x) \int \int d\mathbf{u} d\mathbf{u}' \beta_{S,L} \Psi_S(\mathbf{u}) \Psi_L(\mathbf{u}') \\ &\left. + x^2 \int \int d\mathbf{u} d\mathbf{u}' \beta_{S,S} \Psi_S(\mathbf{u}) \Psi_S(\mathbf{u}') \right]. \end{aligned} \quad (10)$$

Then, the total free energy of a solution of N rotaxanes, a fraction x of length L and $(1-x)$ of length qL , all with diameter d , is

$$\begin{aligned} \frac{F[\Psi_S, \Psi_L, x]}{Nk_B T} &= \frac{F_0[\Psi_S, \Psi_L, x]}{Nk_B T} + \frac{F_1[\Psi_S, \Psi_L, x]}{Nk_B T} + \frac{F_2[x]}{Nk_B T} \\ &= \ln [N/V] - 1 + x \int d\mathbf{u} \Psi_S(\mathbf{u}) \ln [4\pi \Psi_S(\mathbf{u})] + (1-x) \int d\mathbf{u} \Psi_L(\mathbf{u}) \ln [4\pi \Psi_L(\mathbf{u})] \\ &+ \frac{1}{2} \frac{N}{V} \left[(1-x)^2 \int \int d\mathbf{u} d\mathbf{u}' \beta_{L,L} \Psi_L(\mathbf{u}) \Psi_L(\mathbf{u}') + 2x(1-x) \int \int d\mathbf{u} d\mathbf{u}' \beta_{S,L} \Psi_S(\mathbf{u}) \Psi_L(\mathbf{u}') \right. \\ &\left. + x^2 \int \int d\mathbf{u} d\mathbf{u}' \beta_{S,S} \Psi_S(\mathbf{u}) \Psi_S(\mathbf{u}') \right] + x \ln x + (1-x) \ln(1-x) - x \frac{\Delta E}{k_B T}. \end{aligned} \quad (11)$$

In complete analogy with Onsager's treatment, we replace the orientation distribution functions $\Psi_S(\mathbf{u})$ and $\Psi_L(\mathbf{u})$ with parameters α_S and α_L (Figure 3) that characterise the orientation of rotaxanes in the short (S) and long (L) states,

$$\begin{aligned}\Psi_S &= \frac{\alpha_S}{4\pi \sinh \alpha_S} \cosh[\alpha_S \mathbf{u} \cdot \mathbf{n}], \\ \Psi_L &= \frac{\alpha_L}{4\pi \sinh \alpha_L} \cosh[\alpha_L \mathbf{u} \cdot \mathbf{n}].\end{aligned}\quad (12)$$

This allows us to express the free energy of a solution of N rotaxanes at any concentration c as a function of the fraction x and orientational parameters α_S and α_L . This expression for the free energy is derived and given in [Appendices A and B](#), and is referred to using the notation $F(x, \alpha_S, \alpha_L, c)$. At any given concentration, the orientation of the rotaxanes in their short and long states, as well as the fraction that adjust to the short state will adopt values that minimise the free energy. At the lowest concentration, $c < c_i$, where the solution is in a single isotropic phase, rotaxanes in the short and long states will orient randomly or $\alpha_S = \alpha_L = 0$. The fraction of rotaxanes in the short state in the isotropic solution of concentration c is determined by that value of $x(c)$ that satisfies $\partial F(x, \alpha_S = 0, \alpha_L = 0, c) / \partial x = 0$. At high concentration $c > c_a$, where a single nematic phase exists, all rotaxanes are oriented, although rotaxanes in the long state will be more highly oriented than those in the short state. The orientation of the short and long switch states, $\alpha_S(c)$ and $\alpha_L(c)$, as well as the fraction of short switch states $x(c)$, will adopt values that minimise the free energy and are determined by the solution of the 3 equations

$$\frac{\partial F(x, \alpha_S, \alpha_L, c)}{\partial x} = \frac{\partial F(x, \alpha_S, \alpha_L, c)}{\partial \alpha_S} = \frac{\partial F(x, \alpha_S, \alpha_L, c)}{\partial \alpha_L} = 0.$$

Between two critical concentrations, c_i and c_a , the free energy is minimised simultaneously by two sets of $\{\alpha_S, \alpha_L, x\}$: this corresponds to the coexistence of two phases, an isotropic phase and an (anisotropic) nematic phase. The isotropic phase with N_i rotaxanes and volume V_i , with fraction x rotaxanes in the short state and parameters $\alpha_S = \alpha_L = 0$, has a free energy per molecule of $F_i = F(N_i, V_i, x(c_i), \alpha_S = 0, \alpha_L = 0)$. In the nematic phase, the free energy per rotaxane is $F_a = (N_a, V_a, x(c_a), \alpha_S(c_a), \alpha_L(c_a))$. The relative amounts of the phases vary within the concentration range and this is determined by equating the chemical potential of the rotaxanes (irrespective of their state) in each of the phases, as well as the osmotic pressure in each phase.

IV. RESULTS AND DISCUSSION

The free energy expression (Eq. (11)) provides numerical results which yield the phase diagram of these liquid crystalline rotaxanes as a function of the length ratio, q , that is associated with the molecular design of the rotaxane. As stated previously, the phase diagram is similar to that of a system of fixed-length rods, in that there are three different regimes: isotropic; coexisting isotropic and nematic and pure nematic. The concentrations at which each of these regimes occur, are different to the fixed-length case, as we detail later. The system seems rather complicated, since we can

vary two different parameters externally. These are the scaled concentration $\frac{\pi}{4} c L^2 d$ and the ratio of the long to short states, q . Moreover, we have three different regimes (isotropic, nematic, and coexisting), and in each of these regimes, we can measure the order parameter, S for each of the different lengths, and the fraction of short rotaxanes x . Against this apparent complexity is the fact that the free energy is a simple sum of 4 terms. These are: the orientational entropy; the interaction term; the configurational entropy; and the energetic bias. The behaviour of the system can be understood as a competition between all of these terms. We present the results under a number of subheadings: the fraction of short states, the critical concentrations, and the order parameters.

A. Fraction of short states

First we consider a solution of unbiased ($\Delta E = 0$) rotaxanes with $q = 1.1$, and consider the fraction of short states, x , as we increase the total concentration, c , Figure 4. In the limit of infinite dilution, when the rotaxanes orient freely and randomly, the proportion of rotaxanes in the short state, x , is determined by the energy bias in between the states and the configurational entropy, Eq. (7), and is $x = 0.50$ for $\Delta E = 0$, independent of q . As the total concentration increases towards c_i , the molecules begin to interact and in order to maximise translational and orientational entropy, the rotaxanes increasingly adopt a short state at the expense of the configurational entropy. As we will see, this growth in the population of short states is more dramatic, as the ratio of long to short lengths, q increases—this is because switching a randomly oriented long rod to a randomly oriented short rod, increases the translational entropy of the solution. At a critical concentration, c_i , partial orientational ordering occurs and a nematic phase appears which coexists with the isotropic phase. The fraction of short rods in the coexisting phase is x_i for the isotropic phase and x_a for the nematic phase. This nematic or orientationally ordered phase has a larger fraction of rotaxanes in the long state than the coexisting isotropic phase ($x_a < x_i$)—this is because the translational entropy penalty in the nematic phase is reduced by alignment. In an isotropic phase, the randomly oriented long rod would greatly reduce translational entropy (due to collisions) at $c < c_i$, whereas collisions within a nematic phase are significantly less because the molecules are already well-aligned. As in the case of monodisperse rods, these coexisting phases persist over a range of concentrations $c_i < c < c_a$. As the total concentration, c , changes within this range, the concentrations of each phase and the fraction of rotaxanes in the short state within each phase do not change—only the relative amounts of isotropic and nematic phases change. At a total concentration of c_a , the isotropic phase disappears entirely leaving a single nematic phase which grows more ordered with concentration. Because of this, the length of the rods becomes less and less relevant (collisions become rarer for well-aligned systems), and there is not much translational entropy to be gained by being short. The configurational entropy again comes to the fore, and at large enough concentrations, we expect x to approach its “natural” value of 1/2.

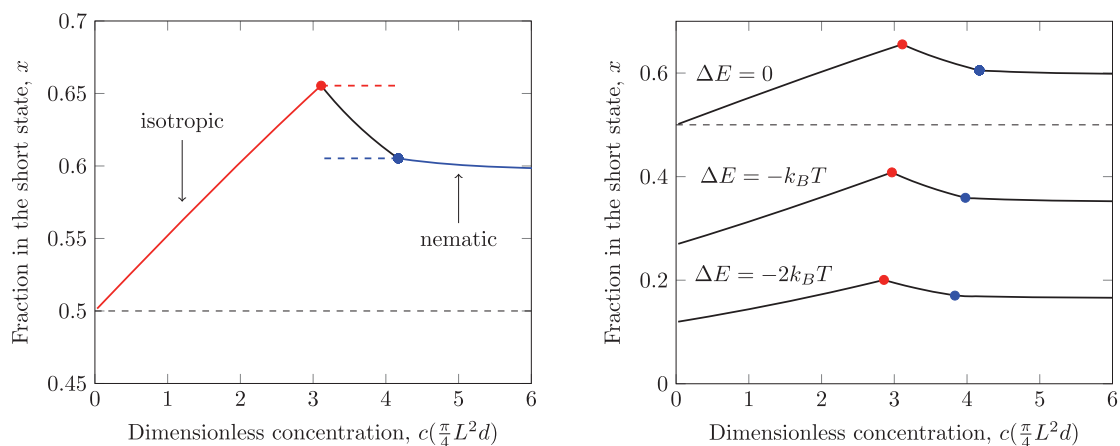


FIG. 4. Left: The fraction of rotaxanes in the short state, x , as a function of dimensionless concentration, $\frac{\pi}{4}cL^2d$, for unbiased rotaxanes ($\Delta E = 0$) and $q = 1.1$. The solid line gives the fraction of short rods in the solution where we use red to denote the isotropic phase and blue for the orientationally ordered or nematic phase. At and above a critical concentration c_i (red circle), the rotaxanes are in coexisting isotropic and nematic phases, with the fraction of short states differing in the coexisting isotropic (dashed red line) and nematic (dashed blue line) phases. As the total concentration increases within the coexistence region, the nematic phase grows at the expense of the coexisting isotropic phase and the overall fraction of short states decreases. At a critical concentration c_a (blue circle), the coexisting isotropic phase vanishes leaving a single nematic phase. The fraction of short states in the nematic phase decreases slightly with increased concentration and in the limit of very large concentrations, the fraction of short states is determined by the bias in the switch states, which for $\Delta E = 0$ is $x = 0.50$ (dashed black line). Right: The fraction of rotaxanes in the short state, x versus $\frac{\pi}{4}cL^2d$ for $q = 1.1$ in the presence of an intrinsic energy bias towards long states. From top to bottom, these are $\Delta E = 0$ (unbiased), $\Delta E = -k_B T$, and $\Delta E = -2k_B T$ (chemical bias towards long states). When the energy bias $|\Delta E|$ becomes much greater than $k_B T$, the variation in x with concentration disappears, that is there is a lack of adaptivity, and the rotaxanes are effectively of fixed length.

We now introduce an energetic bias between the short and long states by having $\Delta E \neq 0$. In Figure 4, we compare the fraction of rotaxanes in the short state versus the concentration for the unbiased case $\Delta E = 0$ with two cases where there is chemical bias towards the long state, $\Delta E = -k_B T$ and $\Delta E = -2k_B T$. The phase behaviour is similar to that in the unbiased case except that the fraction of short rods at infinite dilution, $x(c \rightarrow 0) = \exp[-\frac{\Delta E}{k_B T}]/(1 + \exp[-\frac{\Delta E}{k_B T}])$ is significantly reduced and switching between states is significantly reduced with an increased bias towards long states. Likewise if the short state is energetically preferred, $0 < \Delta E$, there will also be minimal switching. Indeed, without adaptive switching $|\Delta E| \gg k_B T$, the molecules become fixed-length rods with liquid crystalline phase diagram approaching that of Onsager's. If an external switch is applied to these non-adaptive rotaxanes, the rotaxanes can be forced into an Onsager-like liquid crystalline phase behaviour predicted by He *et al.*²²

We now look at the effect of the length ratio q upon the fraction of rods in the short state. This is shown in Figure 5 where we plot x , as a function of concentration, $c(L^2d)^{-1}$, for unbiased rotaxanes for q ranging between 1.1 and 2.0. As noted before, as q increases, the variation in the fraction of short states becomes more dramatic for $c < c_i$. Except in the limits of $c \rightarrow 0$ and $c \rightarrow \infty$ where $x = 0.50$ for all values of q , the fraction of rotaxanes in the short state increases with q at a fixed c . In essence, this system has a choice between a short state and a long state. Short states always have less translational entropy penalty and thus are always favoured whenever there is the possibility of rotaxane overlap. Rotaxane overlap is not possible at infinite dilution, $c = 0$. In the case of highly concentrated solutions, within the Onsager approximation, there is perfect order, and the approximation for the excluded volume interaction gives no overlap. Hence, in both of these cases, $c \rightarrow 0$ and $c \rightarrow \infty$, q becomes irrelevant.

Apart from these numerical results, for the isotropic state, it is possible to produce some analytic results, valid for low concentrations. These will tell us how the fraction of short rods depends on concentration, energy bias, and length ratio. We start from the free energy per rod in the isotropic phase (ignoring irrelevant terms)

$$\frac{F}{Nk_B T} = x \ln x + (1-x) \ln(1-x) + \frac{\pi c L^2 d}{4} \left[x^2 + 2qx(1-x) + q^2(1-x)^2 \right] - x \frac{\Delta E}{k_B T}. \quad (13)$$

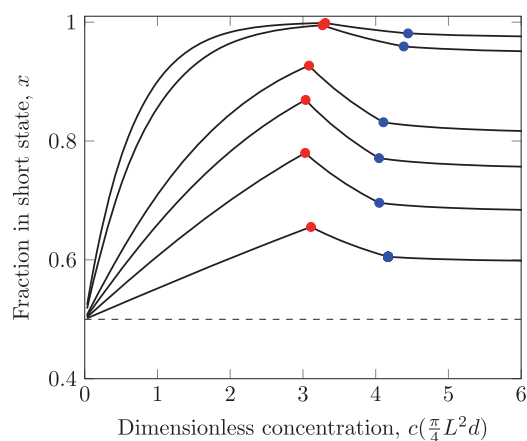


FIG. 5. The fraction of rotaxanes in the short state, x , as a function of the scaled concentration, $\frac{\pi}{4}cL^2d$ for unbiased rotaxanes ($\Delta E = 0$) and (bottom to top) $q = 1.1, 1.2, 1.3, 1.4, 1.8$, and 2.0 . As the ratio of the lengths of the long to short states increases, we see a strong tendency to favour short rotaxanes. In the limit of $c \rightarrow 0$ and $c \rightarrow \infty$, the fraction of rotaxanes in the short state goes to $x = 0.50$ in the unbiased $\Delta E = 0$ case. At intermediate concentrations, the fraction in the short state increases with q , irrespective of phase or coexistence.

In the case of no bias $\Delta E = 0$ and zero concentration, this free energy is minimised when the fraction of short rotaxanes is $\frac{1}{2}$. At non-zero concentrations, we expand the free energy with respect to x about $x = \frac{1}{2}$ and to lowest order in c , minimising gives

$$x = \frac{1}{2} + \frac{\pi L^2 d}{16} c (q^2 - 1). \quad (14)$$

We are thus able to conclude that in the isotropic phase, the fraction of short rods grows linearly with the concentration. Moreover we also have the dependence on q from this equation. A similar procedure allows the dependence on ΔE to be included, but the results are more lengthy.

B. The effect of length ratio

The critical concentrations c_i and c_a , as well as the fraction of short states in the coexisting phases, x_i and x_a , depend critically upon the length ratio, q . First, it is important to recognise that the case of $q = 1$ corresponds to rotaxane states whose lengths are indistinguishable; that is, $q = 1$ is the same as the case of monodisperse rods where $c_i = 3.34(\frac{\pi}{4}L^2d)^{-1}$ and $c_a = 4.49(\frac{\pi}{4}L^2d)^{-1}$.

Figure 6 shows the critical concentrations c_i and c_a versus q for unbiased rotaxane states and the corresponding fraction of short states, x , in each of the coexisting phases versus q , again for the unbiased switch states. Taken together, these

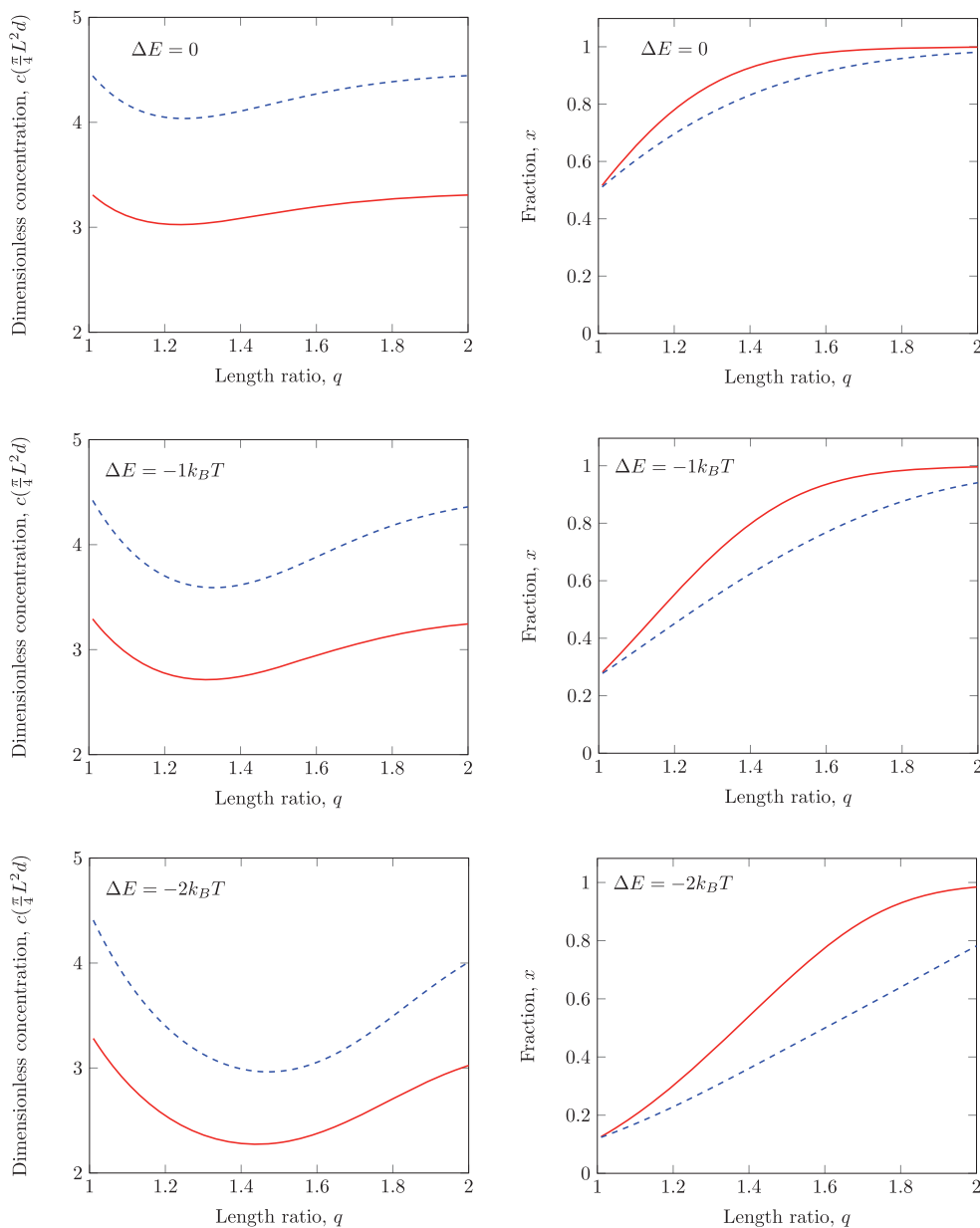


FIG. 6. Left: The critical concentrations as a function of the length ratio of long to short states for different values of the energy bias. The full line is for the isotropic to nematic-isotropic coexistence transition. The dotted line is for the transition from coexistence to pure nematic. At the top is the case $\Delta E = 0$ (no intrinsic bias towards long or short). At middle $\Delta E = -1k_B T$ (a slight bias towards long rods). At the bottom, $\Delta E = -2k_B T$ (stronger bias towards long rods). Right: The fraction of rods in the short state (right) at coexistence, as a function of the length ratio of long to short states for different values of the energy bias. The solid line is the fraction in the isotropic phase, and the dotted line is the fraction in the nematic phase. The values of ΔE are the same as for the left graphs. Two things are notable on these graphs. First the critical concentrations exhibit a minimum as the length ratio increases. Second, for any finite length ratio there is a substantial jump in x between the two different phases.

figures show that the coexistence of isotropic/nematic phases (for $\Delta E = 0$) in the case of large q , ($q > 2$) approaches that of the monodisperse or $q = 1$ case; that is, $c_i(q > 2) \rightarrow c_i(q = 1)$, $c_a(q > 2) \rightarrow c_a(q = 1)$ and $x_i(q > 2) \rightarrow 1, x_a(q > 2) \rightarrow 1$. That is, the coexisting phases become monodisperse in the short state as q increases in the unbiased case. This is because there is no energy bias between long and short states, and (outside of infinite dilution) switching to short states affords more translational entropy than the long state in both the isotropic phase and in the nematic phase. Indeed, even if there is a small chemical bias against short states, Figure 6, the isotropic and nematic phases are dominated by short states when q is significantly large. That is, as we make rotaxanes where q is large, the liquid crystalline phase behaviour is reduced to that of monodisperse short rods, outside of infinite dilution. Rotaxanes designed with too large a value of q do not utilise adaptability in all but the most dilute of concentrations. This contrasts with the case of a mixture of short and long fixed-length rods:^{26,27} the smallest fraction of long rods results in a decrease in the critical concentrations c_i and c_a , and the larger the ratio of the long to short length or q , the more dramatic is this decrease in the critical concentrations.

Figure 6 also shows that rotaxanes which switch between states with $1 < q < 2$ have lower critical concentrations c_i and c_a , and that the critical concentrations are minimal at an intermediate q , q^* . This quantitative result from the free energy model is understood by considering the entropy compromises made when a molecule in a long state switches to a short state. When this happens, there is an increase in translational entropy. This is true if the long rotaxane is randomly oriented in the isotropic phase or oriented in a nematic phase, and this gain in entropy is larger if the difference in lengths of the states is greater. However, when a long state switches to a short state, there is also a penalty paid in configurational entropy, and this penalty is independent of the length of the states. Consequently, for rotaxane states that are nearly of the same length, (q is a little larger than unity), the increase in translational entropy for switching from a long to short state can be small compared to the penalty paid in configurational entropy—and consequently switching from long to short state is not favourable. We already mentioned that adding long fixed-length rods to short rod^{26,27} lowers the critical concentrations c_i and c_a and the larger the length difference between the rods, the lower the critical concentrations. So consequently, for moderate values of q where switching is not entropically favourable, we see a decrease in c_i and c_a with an increase in q towards q^* . Next, as q increases beyond q^* , the length of the long state increases to such an extent that the gain in translational entropy overcomes the penalty in configurational entropy. At these larger values of q , switching is entropically favourable and the rotaxanes readily adopt a short state and the solution trends towards a monodisperse collection of short rotaxane states. The numerical results of the model confirm this: Figure 6 shows that the fraction of short states grows roughly linearly from $q = 1$, but that at large q , the fraction of short states is nearly constant at $x = 1$. Again, from the bidisperse fixed-length molecules, we know that when you decrease the fraction of long

fixed-length molecules, the critical concentrations increase: In analogy, when $q > q^*$, the fraction of short states in both isotropic and anisotropic phases approaches unity and the critical concentrations c_i and c_a increase back to the $q = 1$ limit.

As a final note, it is clear from the graphs in Figure 6 that, provided the inbuilt bias, $|\Delta E|$ is not too large, for large q that almost all the molecules at coexistence are in the short state in the isotropic phase.

C. The order parameter, S

One other quantity of interest is the order parameter, S which quantifies how well-aligned the molecules are. The isotropic state has $S = 0$, and a perfectly aligned nematic phase has $S = 1$. We plot S against the length ratio q in the coexisting phase, for both the long and the short states in Figure 7. For the long states, these graphs show little that is surprising. The long molecules are better-ordered than the short ones, because a lack of order for the long molecules automatically gives more collisions and a reduction in translational entropy. Moreover, the longer the rod the higher the order.

The order parameter of the short molecules in the coexisting nematic phase exhibits a somewhat more complex behaviour in that it is non-monotonic in q . Again, this is due to a balance between translational and orientation entropy as detailed in the free energy model; however we can understand this in terms of the volume available to a short rotaxane in the nematic phase and Figure 6. When the volume available to an anisotropic rod decreases, it will orient, i.e., S will increase. From Figure 6, the concentration of the coexisting nematic phase, c_a , decreases from $q = 1$ to some q^* , that is, there is *more* volume per molecule in the nematic phase. Rotaxanes in the long state, whose excluded volume grows with q align, and the short rotaxanes, with fewer collisions in a larger molecular volume, are more free to rotate. Consequently, the order parameter for the short state decreases with q for $q < q^*$. However, for $q > q^*$, the concentration of the nematic phase increases with q , and there is *less* volume available to the rotaxanes: rotaxanes in both the short and long state become more aligned and S increases with q for both. This produces the minimum in $S(q)$ for the short state. As we increase q further, the order parameter of the long state increases; however the proportion of long states also vanishes at high q . Again, the disappearance of the long state which has an excluded volume that varies with q^2 , provides additional volume for the growing population of short rotaxanes. With *more* volume per molecule, the rotaxanes in the short state again gain some orientational freedom and their order parameter diminishes. This produces a maximum in $S(q)$ for the short state. However, in the limit of high q , the coexisting nematic phase contains rotaxanes that are entirely in the short state and consequently, it is indistinguishable from the coexisting nematic phase for $q = 1$. That is, for the short state, $S(q \rightarrow \infty) = S(q = 1)$. When the rotaxane has a small intrinsic bias towards the long state, these changes in the order parameter with q become more dramatic, primarily because the variation in the proportion of short rods in coexistence varies more dramatically with q when there is intrinsic bias towards the long state: from Figure 6, we

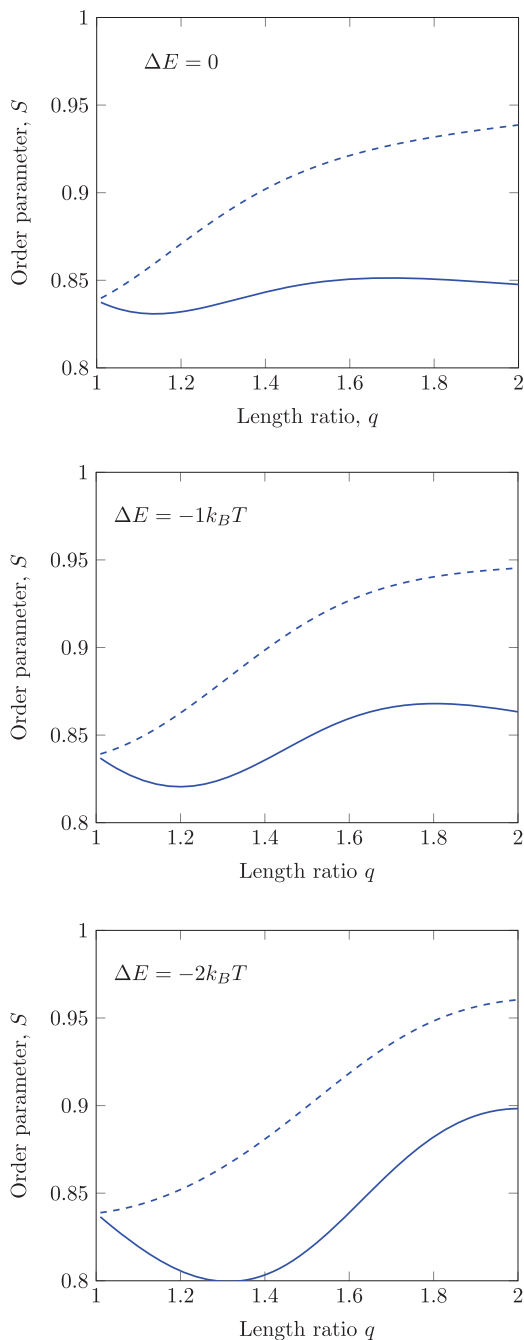


FIG. 7. The nematic order parameter, S for molecules in the short state (full line) and long state (dashed line) in the nematic phase at coexistence, as a function of the length ratio for different values of the energy bias, ΔE . At the top is the case $\Delta E = 0$ (no intrinsic bias towards long or short). At middle $\Delta E = -1k_B T$ (a slight bias towards long rods). At the bottom, $\Delta E = -2k_B T$ (stronger bias towards long rods). Note that the order parameter for long rods always increases, but that for short rods shows a minimum followed by a maximum.

see that $0.5(q = 1) \leq x \leq 1(q \rightarrow \text{large})$ for $\Delta E = 0$, but that $0.15(q = 1) \leq x \leq 1(q \rightarrow \text{large})$ for $\Delta E = -2k_B T$.

V. CONCLUSIONS

Here we examined the phase behaviour of 2-state adaptive rotaxanes. These rotaxanes should be contrasted with those

studied earlier by the present authors,²² where the length was externally controlled. Here the length is chosen by the rotaxane molecule itself in response to the local concentration environment. One major conclusion of this study is that the 2-state adaptive rotaxane forms isotropic and nematic phases, just as the fixed-length rod system does. However, the critical concentrations are different from the fixed-length system, and moreover they show a minimum as the length ratio is increased. In particular, for an unbiased rotaxane ($\Delta E = 0$), it is best to use a length ratio which is small $q \approx 1.2$. Large length ratios, $q > 2$, are counter-productive. The rotaxane has a choice of being of length L or length qL , and if q is made too large, the loss of translational entropy due to collisions becomes prohibitive. In the limit of large q , the system effectively ignores the possibility of having rods of length qL and behaves as if it had rods of fixed short length L .

There is a good reason why we cannot have $q > 2$ with only two axles. This means that such an extension would be geometrically impossible. Of course, we could have larger q values by using more axles per rotaxane, but in such a case, the flexibility of the extended molecule would need to be accounted for.

In the isotropic state, the fraction of short states increases with increasing concentration, because short states undergo fewer collisions. However, once the coexistence regime is entered, the alignment implies fewer collisions and the advantage short states have is reduced. Thus in the coexistence regime, the fraction of short states decreases (because the nematic phase increases in volume), and keeps decreasing when a pure nematic phase comes into being. The initial increase in the fraction of short states (Eq. (14)) is perhaps the simplest experimental test of the theory, because this occurs in the isotropic phase, and does not require the existence of a nematic phase. In particular, the linear increase in x with c should be relatively simple to detect.

One referee has raised the question of our energy biases, ΔE , in particular why they seem to have limited effect on the transition concentrations, and why we do not push them to higher negative values. The reason for their limited effect is that even $\Delta E = -2k_B T$ is not particularly large. For $\Delta E = -20k_B T$, we would expect a large effect. However, if we push $|\Delta E|$ to be large, we encounter a simple problem. The system no longer behaves as adaptive, and becomes one of the rods with a single length. It then reverts to the ordinary Onsager system, and all novelty is lost.

The most unexpected conclusion is that the order parameter for the short state in the nematic shows a minimum and a maximum as the rod length ratio is increased. This might be difficult to detect experimentally, because it requires a measurement of the order of only one species, but it should be easily measured in computer simulation.

An important question to ask is which experimental systems should be used to detect these effects. In the review by Bruns and Stoddart,¹ there are many systems which undergo extensions in the range we are interested in. What is required is one for which the Onsager theory should be approximately true. Such systems tend to have large ratios of length to

diameter. The first test that needs to be made in such cases is to take to axles individually, prior to rotaxane formation, and ensure that at high enough concentration a nematic state is formed.

ACKNOWLEDGMENTS

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APPENDIX A: THE ONSAGER THEORY FOR RODS OF FIXED LENGTH

Here we review Onsager's theory^{19,28} for rods of fixed length L and diameter d . The equilibrium partition function for a solution of N rods with orientational distribution Ψ is

$$Z[\Psi] = \frac{1}{N!} \int_{\Psi} \prod d\mathbf{u}_i \prod d\mathbf{R}_i \exp \left[-\frac{\sum_{i>j} U_{i,j}}{k_B T} \right],$$

where \mathbf{u}_i is the unit vector, directed along the long axis of the i th rod, \mathbf{R}_i is the rod's centre of mass position, and $U_{i,j}$ is the interaction energy between the i th and j th rods. We can rewrite this partition function as a product of functions,

$$Z[\Psi] = Z_0[\Psi] Z_1[\Psi].$$

Z_0 is the partition function associated with distributing non-interacting rods with an orientational distribution $\Psi(\mathbf{u})$, and Z_1 is the contribution from the interactions between the rods, or

$$Z_0 = \frac{1}{N!} \int_{\Psi} \prod d\mathbf{u}_i \prod d\mathbf{R}_i$$

and

$$Z_1 = \frac{\int_{\Psi} \prod d\mathbf{u}_i \prod d\mathbf{R}_i \exp \left[-\frac{\sum_{i>j} U_{i,j}}{k_B T} \right]}{\int_{\Psi} \prod d\mathbf{u}_i \prod d\mathbf{R}_i} \\ = \langle \exp \left[-\frac{\sum_{i>j} U_{i,j}}{k_B T} \right] \rangle_{\Psi}.$$

Z_0 is determined in the following way: the position of each rod can be any location within the volume, so $\int d\mathbf{R}_i = V$ or $\int \prod_i^N d\mathbf{R}_i = V^N$. However, the orientation vectors of the rods are constrained by the distribution $\Psi(\mathbf{u})$. The set of all possible unit-vectors, \mathbf{u} , sweeps out the surface of a sphere, which we divide into small regions of area (or solid angle) Ω . As the rods are oriented according to $\Psi(\mathbf{u})$, then the number of rods oriented within $\mathbf{u}_a \pm d\mathbf{u}_a$, or solid angle of size Ω , is $n_a = N\Psi(\mathbf{u}_a)\Omega$. Thus $\int_{\Psi} \prod_i^N d\mathbf{u}_i$ is evaluated discretely as the number of ways of assigning N rods to a set of differential solid angles, each of size Ω with population n_a or

$$\int_{\Psi} \prod_i^N d\mathbf{u}_i = \frac{N!}{\prod_i n_a!} \Omega^N.$$

Taken together, this yields

$$Z_0 = \frac{(\Omega V)^N}{\prod_i n_a!}.$$

As $\sum_a n_a = N$ and $\sum_a \Omega \Psi(\mathbf{u}_a) = 1$, then the free energy (entropy) associated with distributing non-interacting rods with an orientational distribution $\Psi(\mathbf{u})$ is

$$F_0[\Psi] = -k_B T \ln [Z_0[\Psi]]$$

$$= Nk_B T \left[\ln [N/V] - 1 + \int d\mathbf{u} \Psi(\mathbf{u}) \ln [\Psi(\mathbf{u})] \right]. \quad (\text{A1})$$

The contribution to the free energy from the interactions between rods can also be found from the corresponding partition function, $F_1[\Psi] = -k_B T \ln [Z_1[\Psi]]$, or alternatively, we can make simple use of a simple virial expansion of the free energy written in terms of particle number,

$$F_1[\Psi] = -k_B T \ln \left\langle \exp \left[-\frac{\sum_{i>j} U_{i,j}}{k_B T} \right] \right\rangle \\ = B_2 N + B_3 N^2 + \dots,$$

where B_j is the j th virial coefficient. In dilute solutions of rods, we only need to consider $B_2 N$, first term in the virial expansion which accounts for the pairwise interaction between two rods of orientation \mathbf{u} and \mathbf{u}' ,

$$B_2 N = \frac{N^2 k_B T}{2V} \int d\mathbf{u} d\mathbf{u}' \Psi(\mathbf{u}) \Psi(\mathbf{u}') \beta(\mathbf{u}, \mathbf{u}'),$$

where $\beta(\mathbf{u}, \mathbf{u}')$ is

$$\beta(\mathbf{u}, \mathbf{u}') = \int dR \left[1 - \exp \left[-\frac{U(\mathbf{u}, \mathbf{u}', R)}{k_B T} \right] \right].$$

For a pair of rigid rods which interact as hard bodies (or where the interaction energy is $U = \infty$ when overlapping and $U = 0$ otherwise), $\beta(\mathbf{u}, \mathbf{u}')$ corresponds to the volume that one rod excludes to another rod. For rods of diameter d , but of two different, fixed lengths, L and L^* , the excluded volume for two rods that make an angle $|\gamma| = |\mathbf{u} \times \mathbf{u}'|$ is

$$\beta(\mathbf{u}, \mathbf{u}') = 2LL^*d |\mathbf{u} \times \mathbf{u}'|. \quad (\text{A2})$$

The contribution of pairwise interactions of rods of the same length L to the free energy is

$$\frac{F_1[\Psi]}{Nk_B T} = \frac{1}{2} \frac{N}{V} \int \int d\mathbf{u} d\mathbf{u}' \Psi(\mathbf{u}) \Psi(\mathbf{u}') 2L^2 d |\mathbf{u} \times \mathbf{u}'|. \quad (\text{A3})$$

APPENDIX B: CALCULATION OF THE ADAPTIVE FREE ENERGY

(i) **Free energy of the isotropic phase.** In the isotropic phase,²⁸ all molecules are randomly oriented, irrespective of whether they are in the short or long state, so that the orientational distribution function is a constant, $\Psi_S[\mathbf{u}] = \Psi_L[\mathbf{u}] = \frac{1}{4\pi}$. Consequently, there is no orientational entropy of non-interacting rods in the isotropic phase and $\int d\mathbf{u} \Psi[\mathbf{u}] \ln [4\pi \Psi[\mathbf{u}]] = 0$. To simplify the three terms for the free energy associated with pairwise interactions between rods, we need to specify the excluded volume of pairs of molecules. Let γ be the angle made by two molecules so that we have

$$\beta_{S,S}(\gamma) = 2L^2 d |\mathbf{u} \times \mathbf{u}'| = 2L^2 d |\sin \gamma|, \quad (\text{B1})$$

$$\beta_{S,L}(\gamma) = 2qL^2 d |\mathbf{u} \times \mathbf{u}'| = 2qL^2 d |\sin \gamma|, \quad (\text{B2})$$

$$\beta_{L,L}(\gamma) = 2q^2 L^2 d |\mathbf{u} \times \mathbf{u}'| = 2q^2 L^2 d |\sin \gamma|. \quad (\text{B3})$$

$d\mathbf{u}$ is a differential solid angle, expressible in terms of polar and azimuthal angle or $d\mathbf{u} = d\phi \sin \theta d\theta$. The integrals are of the form

$$\int \int d\mathbf{u} d\mathbf{u}' \beta_{S,S} \Psi(\mathbf{u}) \Psi(\mathbf{u}') = \frac{1}{16\pi^2} \int_0^{2\pi} d\phi \int_0^{2\pi} d\phi' \int_0^\pi \sin\theta d\theta \int_0^\pi 2L^2 d |\sin\gamma| \sin\theta' d\theta' = \frac{\pi L^2 d}{2},$$

$$\int \int d\mathbf{u} d\mathbf{u}' \beta_{S,L} \Psi_S(\mathbf{u}) \Psi_S(\mathbf{u}') = \frac{\pi L^2 dq}{2},$$

$$\int \int d\mathbf{u} d\mathbf{u}' \beta_{L,L} \Psi(\mathbf{u}) \Psi(\mathbf{u}') = \frac{\pi L^2 dq^2}{2}.$$

These are readily performed by rotating the coordinate system so that one rod always lies along the z axis. The free energy of the isotropic phase of concentration c with fraction of short rotaxane states x is

$$\begin{aligned} \frac{F_{\text{isotropic}}}{Nk_B T} &= \frac{F_{0,\text{isotropic}}}{Nk_B T} + \frac{F_{1,\text{isotropic}}}{Nk_B T} + \frac{F_{2,\text{isotropic}}}{Nk_B T} \\ &= \ln\left[\frac{N}{V}\right] - 1 + x \ln x + (1-x) \ln(1-x) + \frac{N}{2V} \left[x^2 \frac{\pi L^2 d}{2} + 2x(1-x) \frac{\pi L^2 dq}{2} + (1-x)^2 \frac{\pi L^2 dq^2}{2} \right] - x \frac{\Delta E}{k_B T} \\ &= \ln c - 1 + x \ln x + (1-x) \ln(1-x) + \frac{\pi c L^2 d}{4} \left[x^2 + 2qx(1-x) + q^2(1-x)^2 \right] - x \frac{\Delta E}{k_B T}. \end{aligned}$$

(ii) **Free energy of the nematic phase.** In the nematic phase, molecules are oriented and those in the long state will be oriented more strongly than those in the short state. We use the angle, θ , that the molecule makes with a director as a measure of the orientation and define two orientational distribution functions, one for the short state, $\Psi_S(\theta)$ and another for the long state, $\Psi_L(\theta)$, using Onsager's trial function, Eq. (2) with $\mathbf{u} \cdot \mathbf{n} = \cos \theta$,

$$\Psi_S(\theta) = \frac{\alpha_S \cosh(\alpha_S \cos \theta)}{4\pi \sinh(\alpha_S)}, \quad (\text{B4})$$

$$\Psi_L(\theta) = \frac{\alpha_L \cosh(\alpha_L \cos \theta)}{4\pi \sinh(\alpha_L)}. \quad (\text{B5})$$

The orientational entropy contribution associated with distributing non-interacting rods in the nematic phase,

$F_0[\Psi, x]$, is then

$$\int d\mathbf{u} \Psi_S(\theta) \ln 4\pi [\Psi_S(\theta)] = \log(\alpha_S \coth \alpha_S) - 1 + \frac{\arctan(\sinh \alpha_S)}{\sinh \alpha_S}, \quad (\text{B6})$$

$$\int d\mathbf{u} \Psi_L(\theta) \ln 4\pi [\Psi_L(\theta)] = \log(\alpha_L \coth \alpha_L) - 1 + \frac{\arctan(\sinh \alpha_L)}{\sinh \alpha_L}. \quad (\text{B7})$$

As in the isotropic case, the three terms for the free energy associated with pairwise interactions between rods can be readily calculated by rotating coordinates. However, unlike the isotropic case, the orientation distribution function, Ψ , is no longer a constant but depends upon θ as well as the state of the rotaxane, long or short.

$$\int \int d\mathbf{u} d\mathbf{u}' \beta_{S,S} \Psi_S[\mathbf{u}] \Psi_S[\mathbf{u}'] = \int_0^{2\pi} d\phi \int_0^{2\pi} d\phi' \int_0^\pi \sin\theta \Psi_S[\theta] d\theta \int_0^\pi 2L^2 d |\sin(\gamma)| \sin\theta' \Psi_S[\theta'] d\theta' = \frac{2L^2 d I_2(2\alpha_S)}{(\sinh \alpha_S)^2}, \quad (\text{B8})$$

$$\int \int d\mathbf{u} d\mathbf{u}' \beta_{L,L} \Psi(\mathbf{u}) \Psi(\mathbf{u}') = \frac{2q^2 L^2 d I_2(2\alpha_L)}{(\sinh \alpha_L)^2}, \quad (\text{B9})$$

where I_2 is second order Bessel function.¹⁹ The contribution due to pairwise interaction of molecules of different size is rather involved. Here we simply write down Onsager's result; in his original work, he describes the derivation in great detail, referring to this as the covolume,

$$\begin{aligned} &\int \int d\mathbf{u} d\mathbf{u}' \beta_{S,L} \Psi_S(\mathbf{u}) \Psi_L(\mathbf{u}') \\ &= qL^2 d \sqrt{\frac{\alpha_S + \alpha_L}{2\pi\alpha_S\alpha_L}} \left\{ 1 - \frac{3}{8} \left(\frac{1}{\alpha_S} + \frac{1}{\alpha_L} + \frac{1}{\alpha_S + \alpha_L} \right) + \frac{15}{128} \left[\frac{8}{\alpha_S\alpha_L} - \left(\frac{1}{\alpha_S} + \frac{1}{\alpha_L} + \frac{1}{\alpha_S + \alpha_L} \right)^2 \right] + \dots \right\}. \quad (\text{B10}) \end{aligned}$$

Like Onsager, we ignore the higher order terms in the last expression, so that the free energy per molecule in the nematic phase, F_2 , reduces to

$$\begin{aligned}
\frac{F_2[\alpha_S, \alpha_L, x, c]}{Nk_B T} = & \ln [N/V] - 1 + x \left[\ln (\alpha_S \coth \alpha_S) - 1 + \frac{\arctan (\sinh \alpha_S)}{\sinh \alpha_S} \right] \\
& + (1-x) \left[\ln (\alpha_L \coth \alpha_L) - 1 + \frac{\arctan (\sinh \alpha_L)}{\sinh \alpha_L} \right] + \frac{1}{2} \frac{N}{V} \left[(1-x)^2 \left[2q^2 L^2 d \frac{I_2(2\alpha_L)}{\sinh^2 \alpha_L} \right] + x^2 \left[2L^2 d \frac{I_2(2\alpha_S)}{\sinh^2 \alpha_S} \right] \right. \\
& + 2x(1-x) qL^2 d \sqrt{\frac{\alpha_S + \alpha_L}{2\pi\alpha_S\alpha_L}} \left[1 - \frac{3}{8} \left(\frac{1}{\alpha_S} + \frac{1}{\alpha_L} + \frac{1}{\alpha_S + \alpha_L} \right) \right. \\
& \left. \left. + \frac{15}{128} \left[\frac{8}{\alpha_S\alpha_L} - \left(\frac{1}{\alpha_S} + \frac{1}{\alpha_L} + \frac{1}{\alpha_S + \alpha_L} \right)^2 \right] + \dots \right] \right] + x \ln x + (1-x) \ln (1-x) - x \frac{\Delta E}{k_B T}. \quad (\text{B11})
\end{aligned}$$

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