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Journal Name

Fast Switching from Isotropic Liquids to Nematic Liquid Crystals: Rotaxanes as Smart Fluids

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We examine a solution of rod-like piston-rotaxanes, which can switch their length by external excitation (for example optically) from a short state of length L to a long state of length qL. We show that this solution can exhibit a number of different behaviours. In particular it can rapidly switch from an isotropic to a nematic liquid crystalline state. There is a minimum ratio $q^* = 1.13$ for which transitions from a pure isotropic state to a pure nematic state are possible. We present a phase-switching diagram, which gives the six possible behaviours for this system. It turns out that a large fraction of the phase switching diagram is occupied by the transition from a pure isotropic to a pure nematic state.

A rotaxane is a "wheel and axle" molecule[1–3], where a ring is threaded onto an axle that is capped with stoppers at both ends to prevent the ring from falling off. Such mechanically or topologically interlocked molecules have been synthesized for many years and represent a very active area of chemical synthesis. Chemists have designed these rotaxanes to act as a 2-state switch: they build 2 different "stations" or attractive sites into the axle and entice the ring to reside at one or the other station, depending upon external influences. The external influence, can be due to pH[4] and ion interaction, redox reaction[5], solvent quality, or light[5,6]. Many examples are given in the review by Bruns and Stoddart[5]. A rigid rod attached to the moveable ring provides one way to monitor or control this internal switch: using AFM, Brough et al.[7]

measured the work required to mechanically push a ring off of an attractive station and Sevick & Williams[8] predicted how such a rotaxane, loaded with inert rings that freely translate on the axle, acts as a molecular-scale shock absorber. As the rod is of the same length as the axle (or larger) switching also brings about a considerable change in the dimension of the molecule (Fig. 1) and this switchable molecular size can create interesting new smart fluids. In this communication, we describe quantitatively how a solution of 2-state rotaxane switches, appended with a rigid rods, provides *externally switchable* liquid crystalline phase transitions. There has been some previous work on Liquid crystalline rotaxane systems[9–11], but our study is very different.

Liquid Crystals are solutions of anisotropic molecules which flow like a liquid, but can have phases which possess different degrees of molecular orientation[12]. They come in many different forms. Here we examine a lytotropic system where a solution of rods undergoes the transition. In dilute solutions, the fixed-size anisotropic molecules have no long-range translational or orientational order - the solution of molecules is isotropic. However, with increased concentration a nematic phase appears where the molecules have no long-range translational order, but self-align to have directional order along their long axis[12]. The important point for applications is that the aligned nematic phase is birefringent, and can be easily detected optically using cross polarised filters. This fact, and their alignment by electric fields is the basis of liquid crystalline displays.

The usual transition from isotropic to nematic is based either on increasing the concentration (lyotropics) or decreasing the temperature (thermotropics). In this paper we show that, for a lyotropic system, by keeping the concentration fixed, but switching the rod length, we can easily transition from an optically inactive isotropic phase to a birefringent nematic phase. This gives us a

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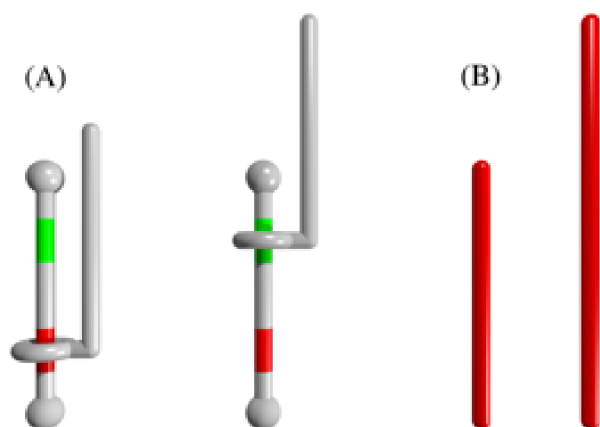
Fig. 1 (A): An illustration of a [2]-rotaxane with attractive stations (denoted by red & green) built into the axle and a rod attached to the interlocked ring in (left) the short state, and (right) the long state. The reversible switching between short and long states provides an added mechanism to switch between an isotropic and a nematic liquid crystalline phases, which exhibit strikingly different optical properties. (B): The simplified model of this structure where a cylinder extends from a length L to a length qL, at fixed diameter d.

system whose bulk optical properties can be externally switched.

Our quantitative calculation is based upon Onsager's classical treatment[13], applied to a simple model of a 2-state rotaxane switch. Onsager's theory assumes a solution of volume-excluding rods where the solvent fills the space surrounding the rods. Alignment of the rods leads to a decrease in rotational entropy but may also increase the volume available for placement of the rod's center of mass, or in other words, may increase the translational entropy. Onsager's theory captures this competition between rotational and translational entropy over a concentration range of rods of fixed length. In our extension of this model, we consider a molecular switch that has two possible states, long and short, depending upon the residential station of the ring With the rod and axle of the same length, and with the stations placed near the ends of the axle, the extent of the molecule can switch from length L to length qL. In our description, we limit the ratio of long to short states to $1 \leq q \leq 2$ although q can be increased beyond 2 by linearly concatemerizing several such switches into a daisy-chain of extendable molecules. We assume that the switching action is 100% efficient: that is, the switches are all in either the short state or long state and there is no mixture of switch states. Analysis of a more complicated "polydisperse" systems is possible[14], but for simplicity is avoided here in this first study.

The physics is essentially as follows. Consider the molecules as hard rods of length L, and diameter d. We assume only hard body interactions between the molecules. The model does have a solvent, but this is implicit, just as in the Flory theory for polymers - the effect of all the solvent and rod interactions is assumed to produce a hard-body interaction between the rods. The model does not rely on the chemical details of the solvent or the rods, and encompasses any system with effective hard-body interactions. At low concentrations c (number of molecules per unit volume), the molecules do not touch each other and do not interact. They thus minimise their free energy by maximising their entropy. Each rod has both translational entropy (associated with where in space its centre of mass is located), and rotational entropy (associated with the direction in which it points in space). At low c the cylinders thus are found distributed randomly throughout their container and point in random directions. This is the isotropic state. At higher concentrations the cylinders begin to interact. However, we have hard-body interactions and no overlaps are allowed. We now imagine two rods which are close to each other. The hard-body interactions imply that the only terms in the free energy are entropic. When two cylinders approach each other they suffer an excluded-volume interaction, which decreases their translational entropy. This penalty is lower if the angle between the cylinder axes, γ, is small, i.e. if they are closely aligned. The cylinders can thus increase their translational entropy by aligning. However, aligning, by definition decreases their rotational entropy, and they are now restricted in the directions they can point. In order to maximize the total entropy the cylinders adopt a compromise, and some alignment is the result. Because all the cylinders can interact in this way this produces a system where all the cylinders align roughly along one direction, producing a nematic phase. The degree of alignment is never perfect, but it increases as the concentration increases.

Experiments, computer simulation, and theory show that the transition from isotropic to nematic is 1st order, so there is a sudden jump in alignment from 0 to some finite value at critical concentration c_1. Moreover there is always a coexistence regime, where isotropic and nematic states coexist in a single sample. Furthermore the concentration of molecules in the nematic state, c_2, is always greater than c_1. By gradually increasing c the following behaviour is observed. At small c the whole sample is isotropic. As c is increased the whole sample remains isotropic until c is slightly greater than c_1. At this point a small volume becomes nematic. Further small increases in c does not change the concentration in either phase, it remains at c_1 and c_2. All that occurs is that the volume of the nematic phase gradually grows at the expense of the isotropic phase. Eventually when $c = c_2$ the entire sample is nematic. Beyond this point any further increase in concentration leads to nematic phase with the concentration c.

This system is analogous to that of a hard sphere fluid with attractive interactions between the spheres. For a closed container,

at low densities a gas phase is formed. As more material is added the gas density increases, until at a critical density a small section of the liquid phase forms in coexistence with the gas phase. As still more material is added the liquid phase increases in size but the gas and liquid phases each have constant density. Eventually all the container is liquid, and further addition of material merely increases the density of the liquid. The gas phase corresponds here to the isotropic phase, and the liquid phase to the higher density nematic phase.

We will not reproduce the calculation for the concentrations c_1 and c_2 here[13–15]. We note in passing that the excluded volume between two rods at an angle γ is $2L^2d|\sin\gamma|$. This is very different from the volume of a rod $\frac{\pi}{4}d^2L$, by a factor of $\sim L/d$, so that in the isotropic state a rod affects a volume much larger than its actual volume . We would thus expect that the critical concentrations c_1 and c_2 would be roughly $\sim 1/(L^2d)$. We shall use the results of the exact numerical solution[14]:

$$c_1 = 3.290(L^2d)^{-1} \quad c_2 = 4.191(L^2d)^{-1} \tag{1}$$
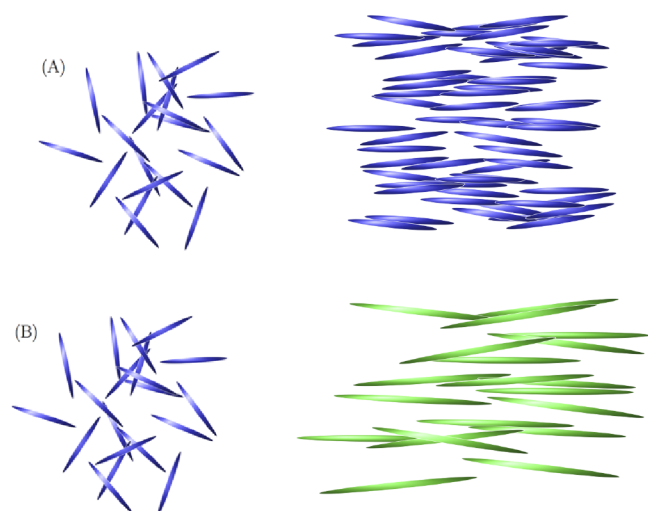
Fig. 2 The initial isotropic phase (left) and final nematic phase (right) associated with (A) increasing molecular concentration at fixed molecular length, and (B) increasing molecular length at fixed molecular concentration. At left is the isotropic phase, where the rods point in all directions. At right is the nematic phase where the rods preferentially point in one direction. This transition is usually accomplished by increasing the concentration, as in (A). Here we show that it is possible to switch between isotropic and nematic by increasing the rod length (B), via the use of a rotaxane.

It is helpful to define dimensionless critical concentrations as $c_1^* = c_1L^2d = 3.290$ and $c_2^* = c_2L^2d = 4.191$. This classical Onsager treatment tells us that for monodisperse molecular cylinders, there is a purely isotropic phase for the concentration range $0 < c < c_1$, an isotropic-nematic phase coexistence region for

$c_1 < c < c_2$, and a purely nematic phase for $c > c_2$. Thus, to affect a transition between phases one uses the rather slow process of increasing the concentration of molecules of fixed length (Fig. 2A). A solution of rotaxane-based switches potentially allows an entirely different and much more rapid way of transforming between phases. Rather than changing the concentration of molecules, we simply switch each molecule to its more extended or long state, or back again to its short state, to transform reversibly between the phases, (Fig. 2B).

To illustrate this, we use a very simple model of a rotaxane-based switch (Fig. 1B). We let each rotaxane be represented by a cylinder whose length is either L or qL, i.e. it increases by a factor q. The cylinder diameter is fixed at d. The only other parameter is the the dimensionless number concentration of cylinders $c^* = cL^2d$.
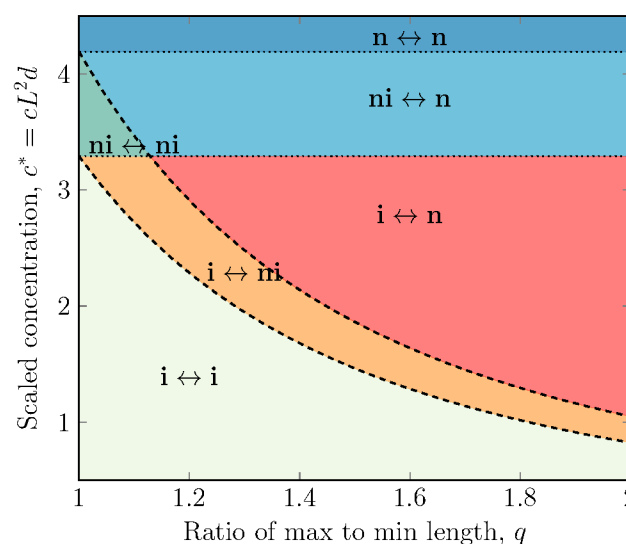
Fig. 3 The phase-switching diagram for this system. We have plotted the scaled concentration versus the ratio of the two lengths. There are three possible initial states (isotropic (i), coexisting isotropic and nematic (ni), and pure nematic (n)) and the same final states, leading to six possible regions in the switching diagram. Although most of the regions will show a change in optical contrast using crossed polars, the region of most interest is shaded in red, where a transition from pure isotropic to pure nematic is predicted.

The initial system, before switching is a monodisperse collection of cylinders of length L, diameter d and concentration c^*. This system could be in three different regimes, depending on the concentration c^* as given by equation (1). For low concentrations $c_L^* < 3.290$ we have a pure isotropic phase, labelled (i). For intermediate concenetrations $3.290 < c_L^* < 4.191$ we have coexisting nematic and isotropic phases, (ni), while for high concentrations, $c_L^* > 4.191$ there is a pure nematic phase (n), or

$$\text{Short State} = \begin{cases} i & c_L^* < 3.290 \\ ni & 3.290 < c_L^* < 4.191 \\ n & c_L^* > 4.191 \end{cases} \quad (2)$$

We now switch the rotaxane to the long state, so that each cylinder now has a length qL, but the same diameter d. The concentration of cylinders is still the same, c, but crucially, the scaled concentration is now $c_{qL}^* = q^2 c_L^*$, i.e. the scaled concentration (which determine the particular regime the system is in), is now a factor of q^2 higher. Again, in the switched state we have the same possible 3 regimes (i, ni, n) depending on c_L^*:

$$\text{Long State} = \begin{cases} i & c_L^* < 3.290/q^2 \\ ni & 3.290/q^2 < c_L^* < 4.191/q^2 \\ n & c_L^* > 4.191/q^2 \end{cases} \quad (3)$$

At constant concentration and upon complete switching of all molecules from short to long states, there are 6 possible reversible transitions: $i \to i$, $i \to ni$, $i \to n$, $ni \to ni$, $ni \to n$, and $n \to n$. Each of these transitions is reversible by switching the molecules back to their short states. We can represent these transitions on what we call a "phase-switching diagram" which given the two parameters q and c_L^* allows us to determine what the initial and final states will be. To draw such a diagram all we need are the two equations (2) and (3). We draw the four curves: $c_L^* = 3.290, 4.191, 3.290/q^2, 4.191/q^2$. These delineate the 6 regions Fig 3.

As can be seen from the switching diagram, all the theoretical processes are in fact possible, i.e. there are 6 regions in the diagram. The most important region is the large region associated with $i \leftrightarrow n$ switching: As this transition is between 100% isotropic and 100% nematic phases, it provides the greatest optical contrast. The bordering $i \leftrightarrow ni$ region is also of interest as the transition is between an 100% isotropic phase and some nematic phase which would also provide optical contrast. The diagram also shows that the minimum length of the long state that is required for the easily observable $i \to n$ transition corresponds to $q_{min} = 1.13$, which can be found by solving $c_L^* = 3.290 = 4.191/q^2$. For a q ratio lower than this, it is not possible to undergo the transition from a pure isotropic to a pure nematic state, although a transition from a pure isotropic to a coexisting nematic-isotropic state is certainly possible. We also see that the $i \leftrightarrow n$ transition occurs at lower concentrations as q, the ratio of extension in the long to short state, increases. Optical contrast is still expected in switching regions $ni \leftrightarrow ni$, $i \leftrightarrow ni$, and $ni \leftrightarrow n$, because each of these regions leads to a change in the fraction of the sample which is in the nematic phase. The transition $n \to n$ might seem like it is rather uninteresting. However, in fact this transition involves an increase in order. The typical angle from which a cylinder deviates from the mean is[13] $\theta \approx 2\pi^{-1/2}(L^2 dc)^{-1}$. Thus by increasing

the length by factor q the angular variation decreases by a factor of q^{-2}. As a general rule, as long as we are not in the region where $i \leftrightarrow i$, we will always see some increase in optical contrast. In other words, to see an increase in contrast we need to have $c_L^* > 3.290/q^2$.

It is important to ask if our model systems have significant overlap with experimentally accessible systems. In particular, we require a ratio of long to short states, q at least of 1.13, in order to see the most startling transition of $i \leftrightarrow n$, i.e. going from no nematic to all nematic. . Bruns and Stoddart[5] have done a survey of molecular switching systems which undergo extension. They list 22 systems (their table 2) with q values ranging from 1.19 to 3. The length cited for ordinary liquid crystals[12] is 300 Angstroms, which is of the same order as many of these listed switching systems. This is good indication that the liquid crystalline switching transitions that we predict are feasible. None of the molecules mentioned by Bruns and Stoddard are perfectly rigid; conformational fluctuations provide flexibility and fluctuations in the length of the axle. However, the theory used here is still valid, provided the molecule does not become very flexible. i.e. the length fluctuations are small in comparison to the change in length caused by the switching of the molecule. The issue of extreme flexibility has been examined by Khokhlov and Semenov[16] and Odijk[15] who have shown that even in the case of polymeric systems with rigid elements connected by flexible spacers, a nematic transition is possible. Moreover, for thermotropic systems there are many examples of main-chain liquid crystalline polymers.

From the experimental point of view it would be useful to have the concentrations in molarity. The typical critical concentration (in units of number of rods per volume) is $c_T = L^{-2}d^{-1}$. If we say that a typical molecule is λ angstroms long and δ angstroms in diameter, then converting from cubic metres to litres gives us the number of molecules per litre as $n_T = 10^{-3}/(\lambda^2\delta 10^{-30})$. The number of moles per litre is then $n_T = 1667/(\lambda^2\delta)$. With $\lambda = 100$ and $\delta = 2$ we find a molarity of $n_T = 0.08$, as the typical scale. With rods 10 times as long, the typical molarity is reduced by a factor of 100.

The model used here still suffers from some well-known limitations. The first is that the rod and axle are parallel to each other. In the case where they are at an angle, or where the angle could fluctuate, the theory would need to be modified. The second, and more involved assumption is that all interactions are those of hard-bodies. Although this is the traditional assumption in lyotropic liquid crystalline systems, in reality there will be dispersion forces between the rods which often promote the formation of liquid crystalline phases. Despite these limitations our calculations suggest that a system of rod-like rotaxanes can form the basis of a solution capable of rapid optical switching.

In conclusion we have shown using a simple model that it

should be possible to switch between isotropic and nematic solutions using a rotaxane system, without changing the concentration. This could be done rapidly, for example using an optical trigger for the switch. In practice this is most likely to be seen with a long molecule which is relatively stiff, which undergoes an extension by at least a factor of 1.2 and cross-polarised filters must be used to see the effect.

References

1 G. Barin, R. S. Forgan and J. F. Stoddart, *Proc. R. Soc. A*, 2012, **468**, 2849–2880.
2 R. S. Forgan, J.-P. Sauvage and J. F. Stoddart, *Chem. Rev.*, 2011, **111**, 5434–5464.
3 L. Fang, M. A. Olson, D. Benitez, E. Tkatchouk, W. A. Goddard, III and J. F. Stoddart, *Chem. Soc. Rev.*, 2010, **39**, 17–29.
4 J. Wu, K. C.-F. Leung, D. Benitez, J.-Y. Han, S. J. Cantrill, L. Fang and J. F. Stoddart, *Angewandte Chemie-International Edition*, 2008, **47**, 7470–7474.
5 C. J. Bruns and J. F. Stoddart, *Accounts of Chemical Research*, 2014, **47**, 2186–2199.
6 S. Tsuda, Y. Aso and T. Kaneda, *Chemical Communications*, 2006, 3072–3074.
7 B. Brough, B. Northrop, J. Schmidt, H. Tseng, K. Houk, J. Stoddart and C. Ho, *Proc. Nat. Acad. Sci. U.S.A.*, 2006, **103**, 8583–8588.
8 E. M. Sevick and D. R. M. Williams, *Langmuir*, 2010, **26**, 5864–5868.
9 N. D. Suhan, S. J. Loeb and S. H. Eichhorn, *JOURNAL OF THE AMERICAN CHEMICAL SOCIETY*, 2013, **135**, 400–408.
10 I. Aprahamian, O. S. Miljanic, W. R. Dichtel, K. Isoda, T. Yasuda, T. Kato and J. F. Stoddart, *BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN*, 2007, **80**, 1856–1869.
11 T. Kato, Y. Shoji, M. Yoshio, S. Yamane and T. Yasuda, *JOURNAL OF SYNTHETIC ORGANIC CHEMISTRY JAPAN*, 2010, **68**, 1169–1174.
12 P. de Gennes and J. Prost, *The Physics Of Liquid Crystals*, Oxford University Press, Oxford, UK, 1993.
13 L. Onsager, *Annals of the New York Academy of Sciences*, 1949, **51**, 627–659.
14 G. Vroege and H. Lekkerkerker, *Reports on Progress in Physics*, 1992, **55**, 1241–1309.
15 T. Odijk, *Macromolecules*, 1986, **19**, 2313–2329.
16 A. Khokhlov and A. Semenov, *Physica A*, 1981, **108**, 546–556.