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Citation: *The Journal of Chemical Physics* **148**, 134905 (2018); doi: 10.1063/1.5022134

View online: <https://doi.org/10.1063/1.5022134>

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Rotaxane liquid crystals with variable length: The effect of switching efficiency on the isotropic-nematic transition

Hao He,^{1,a)} Edith M. Sevick,^{1,b)} and David R. M. Williams^{2,c)}

¹Research School of Chemistry, The Australian National University, Canberra, ACT 2601, Australia

²Department of Applied Mathematics, Research School of Physical Sciences and Engineering, The Australian National University, Canberra, ACT 2601, Australia

(Received 11 January 2018; accepted 14 March 2018; published online 3 April 2018)

We examine a solution of non-adaptive two-state rotaxane molecules which can switch from a short state of length L to a long state of length qL , using statistical thermodynamics. This molecular switching is externally driven and can result in an isotropic-nematic phase transition without altering temperature and concentration. Here we concentrate on the limitation imposed by switching inefficiency, i.e., on the case where molecular switching is not quantitative, leading to a solution of rotaxanes in different states. We present switching diagrams that can guide in the design of rotaxanes which affect a macroscopic phase change. Published by AIP Publishing. <https://doi.org/10.1063/1.5022134>

I. INTRODUCTION

Liquid crystals are comprised of anisotropic or rod-like molecules that can be partially aligned or ordered like a crystal, while simultaneously able to flow like a liquid. Onsager¹ described how a solution of rods, interacting only via hard-body repulsion, can transit from a low concentration isotropic phase to an ordered nematic phase at higher concentrations. This transition is understood in terms of a competition between the translational and orientational entropy of the rods. In the isotropic state, the orientational entropy is maximised, so the rods point freely in every direction. As the concentration of rods increases, this orientational freedom limits the translational freedom of the rods. At a critical concentration, a trade-off occurs: rods begin to align with one another (with a reduction in orientational entropy) so as to increase the translational freedom of the rods. This emerging alignment provides an optical signal; similar to crystals, the aligned nematic phase interacts with polarised light. This lyotropic isotropic-nematic transition, first recognised in cholesterol, also occurs for colloidal particles, such as the tobacco mosaic virus, as well as polymers which are not strictly rod-like but have internal flexibility.²

However, a very different kind of molecule with internal degrees of freedom imparted by mechanical bonding³ can also exhibit liquid crystallinity, but without the required change in concentration. Such mechanical bonds, which consist of a topological linkage of at least two covalent structures, have existed for about half a century.⁴ The original example is a catenane, where two macrocycles or rings are mechanically linked or interlocked together. These molecules were first made statistically in low yield by Wasserman,⁵ but

Sauvage *et al.*^{6,7} revolutionised the synthesis of catenanes and other interlocked molecules with a metal templating method. Another example of an interlocked molecule, which is the focus here, is a rotaxane, or a “wheel” and “axle” molecule, where a ring is threaded onto a molecular axle that is stoppered by a bulky group to prevent de-threading. A rotaxane-switch corresponds to a molecular axle into which attractive stations are built; the ring switches between stations depending upon external factors, including chemical reactions,^{8–10} solvent polarity,¹¹ pH,^{12–16} and light.^{17–19} Bruns and Stoddart²⁰ have recently reviewed a class of length-extending two-state rotaxane switches which can be switched from a short to a long state, where the ratio of lengths in these cited examples can be as high as 3.

In two recent publications, He *et al.*^{21,22} introduced the idea of using a solution of two-state rotaxane switches to affect a switchable liquid crystalline phase. A generic two-state rotaxane, predicted to exhibit lyotropic liquid crystalline phase behavior, is illustrated in Fig. 1. In the case of 100% switching efficiency, or where the two-state rotaxane switches quantitatively between two different lengths, He *et al.*^{21,22} predicted a crystalline phase change that occurs without a change in concentration. However, these molecules usually do not switch quantitatively; i.e., a fraction of the molecules do not switch.^{12,13} Instead, solutions of these two-state rotaxane switches consist of a mixture of long and short rods, and switching changes the relative composition of short to long states.

In this paper, we predict the macroscopic change in liquid crystalline phases that result from the molecular switching of two-state rotaxanes, controlled externally, but where switching is not quantitative. The liquid crystalline phases of binary mixtures of rods of fixed length (and small diameter) were previously predicted by Lekkerkerker *et al.*²³ and Birshtein *et al.*²⁴ who constructed phase diagrams for a mixture of rods of length L and qL ($q > 1$), with different fractions of long rods, x . Here we use those predictions to construct a liquid crystalline phase

^{a)}Electronic mail: u4785782@anu.edu.au

^{b)}Electronic mail: Edie.Sevick@anu.edu.au

^{c)}Electronic mail: D.Williams@anu.edu.au

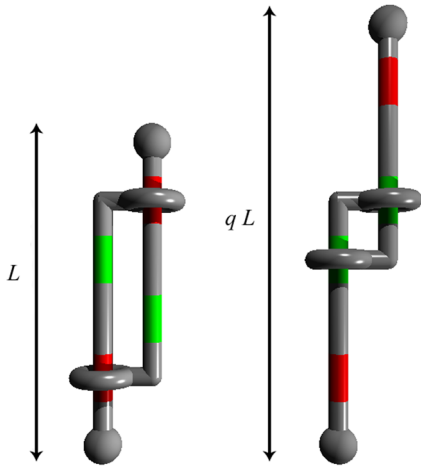


FIG. 1. A two-state rotaxane consisting of two axles or rods interlocked to each other. When the rings are engaged at the red stations, the molecule is in a short state of length L . When the rings are engaged to the green station, the molecule is in a long state of length qL . Switching between long and short states is by external influences such as light or a change in pH which alters the state of minimal energy. We assume that the energy difference in the long and short states is always much greater than $k_B T$, irrespective of which state is minimal. This means that the switch is unaffected by the local alignment or density of molecules. That is, we consider only non-adaptive switches. If the state is affected by the local alignment or density, then the rotaxane switch is adaptive.²² This length switching process provides a possible mechanism to accomplish a direct macroscopic transition from an isotropic to nematic phase, which is not possible in conventional lyotropic liquid crystals without a change in concentration.

switching diagram, predicting the concentration range and q which provides maximal optical signal or when the solution macroscopically switches from isotropic to nematic phases. The remainder of the paper is organised in the following way: First, we briefly review the case of isotropic to nematic phase change with 100% molecular switching efficiency. This provides the framework upon which the incomplete or inefficient switching predictions are constructed. Next, we briefly outline the free energy minimisation or entropy maximisation for binary mixtures of rods. Then we construct switching diagrams for four different switching scenarios to demonstrate the range of concentration and length ratio where observable, macroscopic optical changes can occur by molecular switching.

II. MONODISPERSE RODS

Here we review the thermodynamics of isotropic/nematic phase transition for a solution of monodisperse rods of length L which have no interactions other than hard-body or volume-excluding interactions. This means that the free energy comprises the translational entropy of the rods in solution, the orientational entropy of the rods, and a term that describes the reduction in translational entropy due to the pairwise hard-body interactions. If we let \mathbf{u} be the unit vector specifying the rod direction and $\Psi(\mathbf{u})$ be the orientational distribution so that $\Psi(\mathbf{u})d\mathbf{u}$ is the probability that a molecule has an orientation vector between \mathbf{u} and $\mathbf{u} + d\mathbf{u}$, then the free energy per molecule of a homogeneous solution of N molecules of length L and diameter d in a volume V is

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

Here the term involving $\ln [\Psi(\mathbf{u})]$ is the orientational entropy of the solution, while the final term is the reduction in translational entropy due to pairwise, volume excluding interactions between two rods of orientations \mathbf{u} and \mathbf{u}' . At low concentrations, this free energy is minimised when $\Psi(\mathbf{u}) = (4\pi)^{-1}$ or when all orientations are equally likely and the solution of molecules is isotropic. However, at intermediate concentrations $c_i < N/V < c_a$, two different orientation distributions minimise the energy, indicating that two coexisting phases exist. These two phases are an isotropic phase with $\Psi_i(\mathbf{u}) = (4\pi)^{-1}$ of concentration $c_i = N_i/V_i$ and a nematic phase with preferential orientation, $\Psi_a(\mathbf{u})$, and concentration $c_a = N_a/V_a$. The free energy in the isotropic phase is $F_i = F[N_i, V_i, (4\pi)^{-1}]$; the free energy in the nematic phase is $F_a = F[N_a, V_a, \Psi_a(\mathbf{u})]$. The volume of each phase varies within the concentration range $c_i < c < c_a$, where $c = (N_i + N_a)/(V_i + V_a)$, and is determined by minimising the free energy of the solution, $F = F_i + F_a$, with respect to N_i, V_i , subject to the constraints of $V = V_i + V_a$ and $N = N_i + N_a$. Equivalently, we can determine phase concentrations and volumes by equating the chemical potential of molecules in each coexisting phase (or $\frac{\partial F_i}{\partial N_i} = \frac{\partial F_a}{\partial N_a}$) and equating the osmotic pressure in each phase (or $\frac{\partial F_i}{\partial V_i} = \frac{\partial F_a}{\partial V_a}$).

For a solution of homogenous fixed rods of length L and diameter d , solutions for the critical concentrations, c_i and c_a , have been obtained by numerical minimisation or, as first achieved by Onsager, by parameterisation of the orientational distribution function, $\Psi(\mathbf{u})$. These critical concentrations are reported in units of the inverse average excluded volume of the cylindrical rods or $v_0 = \frac{\pi}{4} L^2 d$, when $L \gg d$. Herein we report dimensionless concentration as $c^* = cv_0$. The values of c_i^* and c_a^* vary slightly with different numerical solutions. Lekkerkerker's solution is $c_i^* = 3.290$ and $c_a^* = 4.191$, that is, the minimum density at which a nematic phase is present is 3.290 molecules per average excluded volume, and the maximum density at which the isotropic phase persists is 4.191 molecules per average excluded volume. For two-state rotaxane switches with external and quantitative (100%) conversion from short to long state, we can compare the isotropic and nematic concentration boundaries (always given relative to the short state, that is, $c^* = cv_0$, where $v_0 = \frac{\pi}{4} L^2 d$) to relate the switching of individual molecules to the switching of liquid crystalline phases. That is, we can compare the isotropic nematic concentration boundaries for solution of homogeneous molecules of short length L ,

$$\text{short state} = \begin{cases} \text{isotropic,} & c^* \leq c_{i,\text{short}}^* = 3.290, \\ \text{nematic-isotropic,} & c_{i,\text{short}}^* \leq c^* \leq c_{a,\text{short}}^*, \\ \text{nematic,} & c^* \geq c_{a,\text{short}}^* = 4.191 \end{cases}$$

to that of a solution of homogeneous molecules of long length, qL ,

$$\text{long state} = \begin{cases} \text{isotropic} & c^* \leq c_{i,\text{long}}^* = 3.290q^{-2} \\ \text{nematic-isotropic} & c_{i,\text{long}}^* \leq c^* \leq c_{a,\text{long}}^* \\ \text{nematic} & c^* \geq c_{a,\text{long}}^* = 4.191q^{-2} \end{cases}.$$

The isotropic to nematic transition provides the dominant optical contrast, so our aim is to identify a concentration, c^* , and a length ratio q , where molecular switching changes the solution from an isotropic to a nematic solution. Initially, the phase of short rods is isotropic, $c^* \leq c_{i,\text{short}}^*$, but after quantitative switching to long rods, the solution is in a nematic phase, or $c^* \geq c_{a,\text{long}}^*$. This corresponds to a solution of two-state rotaxanes of $c^* \leq 3.290$ with a strategic extension ratio of $q > \sqrt{4.49/3.34}$, which provides a first principles approach which can guide synthetic chemists constructing two-state switches with the capacity to phase switch. However most synthesised two-state molecular switches are not quantitative, as a solution of rotaxanes may be in a 80/20 ratio of short to long state; after molecular switching, the ratio may change to a 10/90 ratio of short to long state. How sensitive is the switching of the liquid crystalline phase to the inefficiency of

molecular switching? To address this question, we make use of predictions of the isotropic/nematic transition of a solution of rods of fixed but bidisperse length.

III. A SOLUTION OF RODS OF BIDISPERSE LENGTH

Lekkerkerker *et al.*²³ extended Onsager's treatment to model a solution of rod-like molecules of two different fixed lengths, with a length ratio of long to short rods q , again in the limit of $L \gg d$. Knowing the liquid crystalline phases of a binary mixture of rods of two different fixed lengths allows us to construct a switching diagram of two-state rotaxanes with inefficient molecular switching. The free energy derivation is similar to that for the monodisperse rods,¹ with the exception that we allow the short and long rods to orient differently, or in other words, we have two orientational distribution functions, one for short rods, Ψ_s , and another for long rods, Ψ_ℓ . Additionally, there is a mixing entropy contribution to the free energy, $S_{\text{mix}}/(Nk_B) = x \ln x + (1-x) \ln(1-x)$, where x is the fraction of molecules that are in the long state, of length qL . The corresponding free energy for this solution of rods of bidisperse length is

$$\begin{aligned} \frac{F[N, V, x, \Psi_s, \Psi_\ell]}{Nk_B T} &= \ln \frac{N}{V} - 1 + x \ln x + (1-x) \ln(1-x) + (1-x) \int d\mathbf{u} \Psi_s(\mathbf{u}) \ln[\Psi_s(\mathbf{u})] + x \int d\mathbf{u} \Psi_\ell(\mathbf{u}) \ln[\Psi_\ell(\mathbf{u})] \\ &+ \frac{1}{2} \frac{N}{V} \left[(1-x)^2 \int \int d\mathbf{u} d\mathbf{u}' \Psi_s(\mathbf{u}) \Psi_s(\mathbf{u}') 2L^2 d |\mathbf{u} \times \mathbf{u}'| + 2x(1-x) \int \int d\mathbf{u} d\mathbf{u}' \Psi_s(\mathbf{u}) \Psi_\ell(\mathbf{u}') 2qL^2 d |\mathbf{u} \times \mathbf{u}'| \right. \\ &\left. + x^2 \int \int d\mathbf{u} d\mathbf{u}' \Psi_\ell(\mathbf{u}) \Psi_\ell(\mathbf{u}') 2q^2 L^2 d |\mathbf{u} \times \mathbf{u}'| \right]. \end{aligned} \quad (2)$$

As in the homogeneous, fixed length problem, the critical concentrations are found by determining the orientation distributions that minimise the free energy, and where coexisting phases exist, equating chemical potentials and osmotic pressures of the phases. However, the critical concentrations now depend upon the fraction of long rods, x in the solution. We do not consider the de-mixing of short/long rods, as van Roij and Mulder²⁵ demonstrated that de-mixing within isotropic or nematic phases occurs when the diameter ratio between different rods is more than 5:1. Here, our rods are of fixed diameter irrespective of the short or long state.

The major difficulty in solving Eq. (2) is in approximating the orientational distribution functions for the two kinds of rods, $\Psi_i(\mathbf{u})$, where $i = \{s, \ell\}$. Here we express the orientational vector \mathbf{u} in terms of a shorthand Ω for the spherical polar angles (θ, ϕ) so that the usual normalisation conditions can be written as

$$1 = \int d\mathbf{u} \Psi_i(\mathbf{u}) = \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \Psi_i(\theta, \phi) = \int d\Omega \Psi_i(\Omega), \quad (3)$$

$i = \{s, \ell\},$

and the orientational entropy term in Eq. (2) is written as

$$\int d\mathbf{u} \Psi_i(\mathbf{u}) \ln[\Psi_i(\mathbf{u})] \rightarrow \int d\Omega \Psi_i(\Omega) \ln[4\pi \Psi_i(\Omega)].$$

The contribution to the free energy due to pairwise volume-excluding interactions involves integrals which we identify as ρ_{ij} ,

$$\begin{aligned} \int \int d\mathbf{u} d\mathbf{u}' \Psi_i(\mathbf{u}) \Psi_j(\mathbf{u}') 2L^2 d |\mathbf{u} \times \mathbf{u}'| &\rightarrow \frac{4}{\pi} \\ &\times \int \int d\Omega d\Omega' \sin[\gamma(\Omega, \Omega')] \Psi_i(\Omega) \Psi_j(\Omega') = \rho_{ij}. \end{aligned}$$

Here $\gamma(\Omega, \Omega')$ is the angle made by two rods with orientations Ω and Ω' , where this integral can be written for 3 possible pairings, ρ_{ss} , $\rho_{s\ell}$, and $\rho_{\ell\ell}$, for short-short, short-long, and long-long pairs. Minimising the free energy [Eq. (2)] results in a set of coupled equations

$$\begin{aligned} \ln[4\pi \Psi_s(\Omega)] &= C_s - 2DL^2 c \int d\Omega' \sin[\gamma(\Omega, \Omega')] \\ &\times [(1-x)\Psi_s(\Omega') + qx\Psi_\ell(\Omega')], \\ \ln[4\pi \Psi_\ell(\Omega)] &= C_\ell - 2DL^2 qc \int d\Omega' \sin[\gamma(\Omega, \Omega')] \\ &\times [(1-x)\Psi_s(\Omega') + qx\Psi_\ell(\Omega')], \end{aligned} \quad (4)$$

where the constants C_s and C_ℓ are determined by the normalisation of orientation distribution function, Eq. (3). Equation (4) provides the orientational distribution function of short and long rods, Ψ_s and Ψ_ℓ , for a given concentration, $c = N/V$ and

fraction of long rods, x . Like the monodisperse case, at low concentrations, all orientations are equally likely with $\Psi_s = \Psi_\ell = (4\pi)^{-1}$. But at an intermediate range of concentrations, $c_i \leq c \leq c_a$, there are two pairs of orientation functions that satisfy Eq. (4) indicating coexistence of an isotropic phase, identified with a subscript 1, and a nematic phase, identified with subscript 2. Let c_1 and c_2 denote the concentrations

$$\Pi_1 = \Pi_2$$

$$c_1(1 + c_1[(1 - x_1^2 + 2x_1(1 - x_1)q + x_1^2q^2)]) = c_2(1 + c_2[(1 - x_2)^2\rho_{ss} + 2x_2(1 - x_2)q\rho_{s\ell} + x_2^2q^2\rho_{\ell\ell}]),$$

an equation matching the chemical potential of short rods, $\mu(s)$, in each phase,

$$\mu_1(s) = \mu_2(s)$$

$$\ln c_1 + \ln(1 - x_1) + 2c_1[(1 - x_1) + x_1q] = \ln c_2 + \ln(1 - x_2) + \sigma_1 + 2c_2[(1 - x_2)\rho_{ss} + x_2q\rho_{s\ell}],$$

an equation matching the chemical potential of the long rods, $\mu(\ell)$, in each phase,

$$\mu_1(\ell) = \mu_2(\ell)$$

$$\ln c_1 + \ln x_1 + 2c_1q[(1 - x_1) + x_1q] = \ln c_2 + \ln x_2 + \sigma_2 + 2c_2[(1 - x_2)q\rho_{s\ell} + x_2q^2\rho_{\ell\ell}],$$

as well as one more equation from the mass balance equations

$$cV = c_1V_1 + c_2V_2$$

$$xN = x_1c_1V_1 + x_2c_2V_2.$$

However, these equations, particularly Eq. (4) involving the orientation functions, cannot be solved analytically and researchers have used different numerical methods to obtain solutions. A trial function can be used for Ψ ^{1,26} or one can expand $\sin \gamma$ ²⁷ and solve the system numerically.^{28,29} Here we employ Lekkerkerker's method, as briefly detailed in the [Appendix](#), and approximate the integrals $\rho_{i,j}$ using a 32-point Gaussian integration. The liquid crystalline phase diagram of mixtures of fixed length is obtained numerically, using a Newton-Raphson method, for $0 \leq x \leq 1$ in increments of $\Delta x = 0.01$ with fixed q , as well as for fixed x with the length ratio varying between $q = 1$ (homogeneous rod length) and $q = 2$.

Figure 2 traces the critical concentrations, c_i^* and c_a^* , as a function of the fraction of longer rods in solution for a length ratio of $q = 1.2$ and 2.0 . Note that $x = 0$ corresponds to a monodisperse solution of short rods, recovering the critical concentrations $c_i^* = 3.290$ and $c_a^* = 4.191$. This phase behavior of mixtures of fixed length rods has been predicted in earlier publications,^{23,24} i.e., an isotropic phase (**i**) at small concentrations followed by isotropic-nematic coexistence (**ni**) at intermediate concentrations and a pure nematic phase (**n**) at large concentrations. The phase is determined by three variables: the overall concentration of the solution, c^* , the overall fraction of long rods in the solution, x , and the length ratio, q . The characteristic concentration where the major phase change occurs is near $c^* \approx 3$. Naturally, as the fraction of longer rods increases the concentration boundaries decrease, as it is much easier to form a nematic phase.

of rods in the isotropic and nematic phases and x_1 and x_2 be the fraction of long rods in the isotropic and nematic phases. The coexisting phases at overall concentration c and a fraction of long rods, x , are described by the 6 variables $\{\Psi_{s,2}\Psi_{\ell,2}, c_1, c_2, x_1, x_2\}$ which are determined by Eq. (4) and cast for a nematic phase [as $\Psi_{s,1}\Psi_{\ell,1} = (4\pi)^{-1}$], an equation matching the osmotic pressure in each phase,

A. Switching diagrams

The goal here is to construct a solution of two-state rotaxane switches which will allow us to affect an isotropic to nematic phase transition without changing the concentration of rotaxanes in the solution. That is, our goal is to estimate the concentration range and extension length q , where molecular switching results in a macroscopic change in the orientational phase in solution. As we will show, even for the case of very modest efficiencies in switching on the molecular scale, we still achieve transitions from isotropic to nematic (**i** \rightarrow **n**) and from isotropic to nematic-isotropic coexistence (**i** \rightarrow **ni**). This is important because the presence of a nematic phase, even if the system is not purely nematic, will have an optical effect, and thus the length switching on the molecular scale will induce a macroscopically detectable change in the solution. A weaker optical effect due to molecular alignment occurs for the other transitions between nematic (**n**) and nematic-isotropic coexistence (**ni**) or nematic to nematic (**n** \rightarrow **n**, **ni** \rightarrow **ni**, and **ni** \rightarrow **n**). While these phase transitions can be observed optically, a direct switch from a single isotropic phase to a single nematic phase is of most interest.

As the orientational phase of a solution is determined by 3 parameters, then the switching diagram is determined by four variables: (1) the fixed concentration c^* of the solution, (2) the length ratio, q , of the molecule, (3) the initial fraction of long rods in solution, x_i , and (4) the final fraction of long rods in solution, x_f , after molecular switching. He *et al.*²¹ provided the switching diagram for the case of $x_i = 0.0$ and $x_f = 1.0$, or where switching is quantitative. Here we demonstrate four different switching inefficiencies: where the fraction of long rods changes as $x_i \rightarrow x_f$

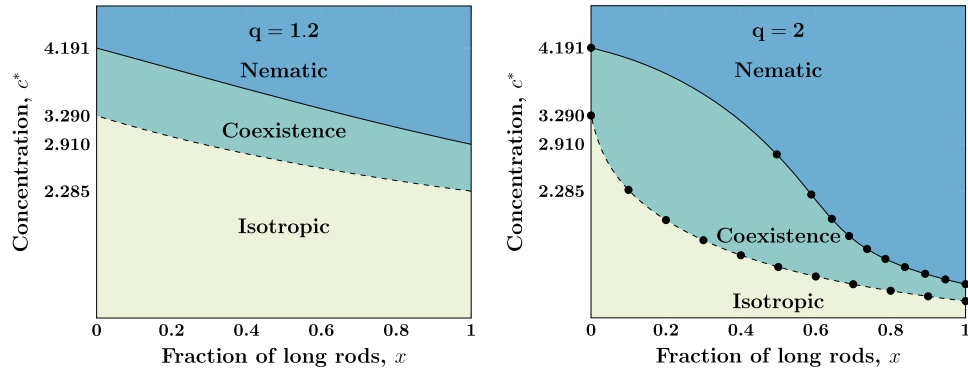


FIG. 2. Scaled concentration, $c^* = cv_0$, versus fraction of long rods for a solution of rods of bidisperse length with a length ratio of long to short of $q = 1.2$ (left) and $q = 2$ (right). The scaled concentration c_i^* (dashed line) separates the isotropic phase region from the region where isotropic and nematic phases coexist: it is the minimum concentration at which a nematic phase is present. The scaled concentration c_a^* (solid line) separates the coexistence region from the single phase nematic region: it is the maximum concentration at which an isotropic phase is present. The data points represent the results of Lekkerkerker.²³ At $x = 0$, corresponding to a solution of short rods of homogeneous length L , $c_i^* = 3.290$, and $c_a^* = 4.191$. The addition of longer rods reduces the concentration range over which an isotropic phase is present and increases the range over which a nematic appears. A large extension ratio q steepens the boundary curves, enhancing the nematic phase with an increase in population of the longer rod of length qL .

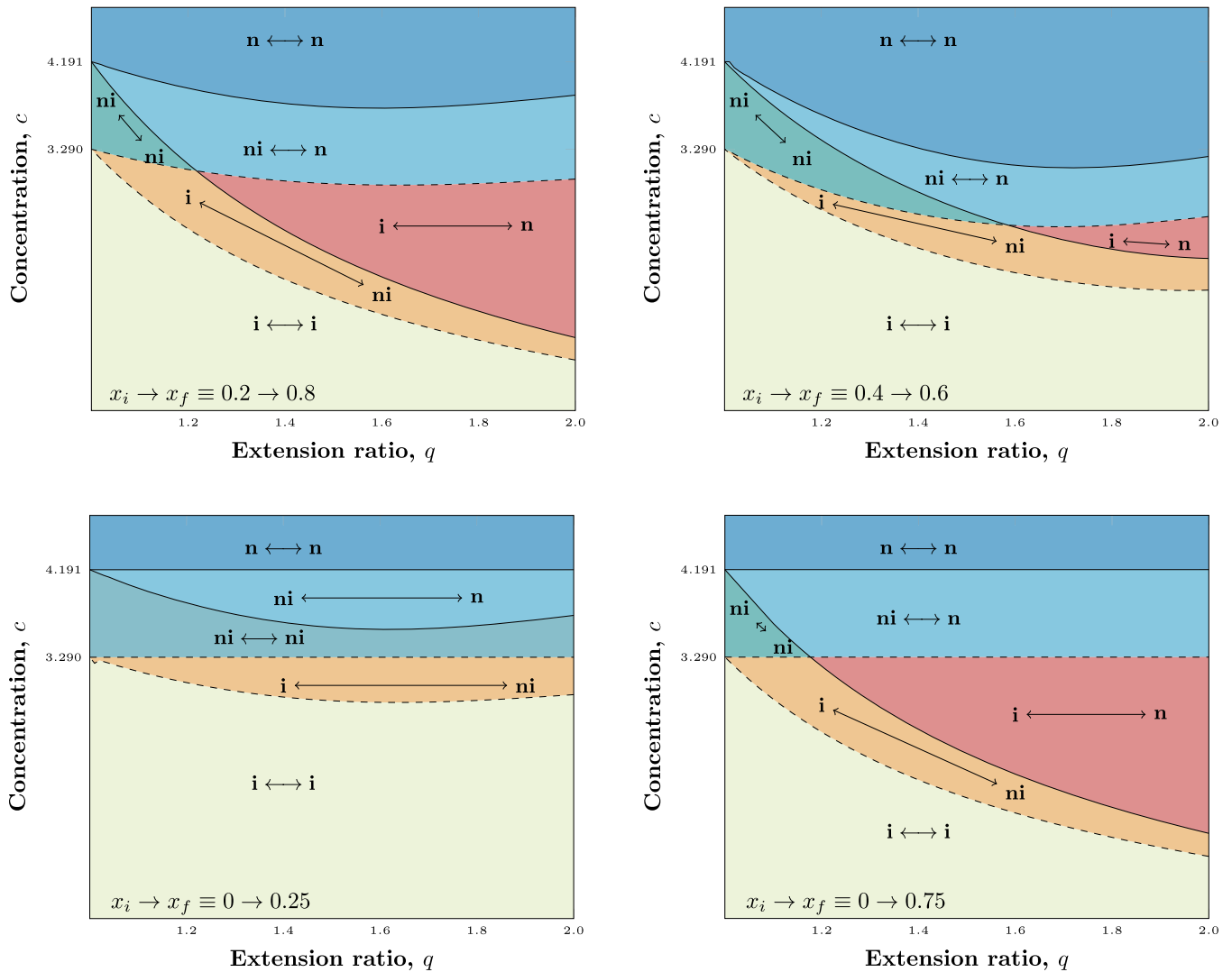


FIG. 3. The switching diagram, scaled concentration, c^* , versus extension ratio q with switching efficiency of $x_i = 0.2 \rightarrow x_f = 0.8$ (top left), $x_i = 0.4 \rightarrow x_f = 0.6$ (top right), $x_i = 0 \rightarrow x_f = 0.25$ (bottom left), and $x_i = 0 \rightarrow x_f = 0.75$ (bottom right). Isotropic (i), coexisting isotropic-nematic (ni), and nematic (n) phases are labeled. Dashed lines separate isotropic and coexistence regions and solid lines separate coexistence and nematic regions, for both initial solution of x_i and final solution x_f . In this way, (i \rightarrow ni) indicates an isotropic phase at x_i switches to an isotropic-nematic coexistence phase at x_f . While a transition from isotropic to coexistence (i \rightarrow ni) or coexistence to nematic (ni \rightarrow n) can show change in optical properties, the transition from pure isotropic directly to a nematic phase is of most interest.

1. $x_i \rightarrow x_f \equiv 0.2 \rightarrow 0.8$
2. $0.4 \rightarrow 0.6$
3. $0 \rightarrow 0.25$
4. $0 \rightarrow 0.75$.

These cases are chosen because they all represent considerably less than 100% switching efficiency, and in two of the cases, the change in x is small, $\Delta x = 0.2$ or 0.25 , corresponding to poor switching efficiency. Figure 3 shows these cases over a limited range of length ratio, $1.0 \leq q \leq 2.0$. These are constructed by overlapping phase diagrams of the initial solution of x_i and final switched solution of x_f .

For three of these cases, the transition from isotropic to pure nematic can be induced in this system by switching the length of the molecules, even for the case of a very modest change in x roughly at $c^* \approx 3$. A high switching efficiency ($\Delta x = x_f - x_i$ is large) creates a significant difference in the critical concentrations, facilitating $\mathbf{i} \leftrightarrow \mathbf{n}$ transitions of a greater range of q (as demonstrated by cases $0.2 \rightarrow 0.8$ and $0 \rightarrow 0.75$). When the switching efficiency is relatively low, for example, $x_i = 0 \rightarrow x_f = 0.25$, switching in molecular length is not enough to trigger a direct transition from isotropic to nematic phase with a reasonable extension ratio q . Importantly this is not the least efficient switch case: the case of $0.4 \rightarrow 0.6$ has a lower switching efficiency ($\Delta x = 0.2$) but still demonstrates a significant $\mathbf{i} \rightarrow \mathbf{n}$ phase switch because of the initial presence of long rods. This suggests that not all molecules incorporated need to be designed as switchable in order to achieve a macroscopic phase transition. For example, the same phase switching predicted for the inefficient switching case of $0.4 \rightarrow 0.6$ also holds for a solution mixture containing 40% *fixed-length* long (qL), 40% *fixed-length* short (L) molecules, and only 20% molecules that quantitatively switch from $L \rightarrow qL$. What the switching diagram does show is that even for this case of very modest changes in switching on the molecular scale (either inefficient switching or a small fraction of quantitative switches), we still get transitions from isotropic (\mathbf{i}) to nematic-isotropic coexistence (\mathbf{ni}).

IV. CONCLUSIONS

We have constructed the macroscopic isotropic-nematic phase switching diagram for a rod-like molecule that can switch between two different lengths via a mechanical bond. We have previously studied this system in the case where the microscopic switching in length was 100% efficient, i.e., all the molecules switch quantitatively between short and long states. Here we have examined the more realistic case of an inefficient system where molecular switching is not quantitative. We have shown that the macroscopic, switchable phase transition from isotropic to nematic is in fact fairly robust and can be found even for cases of very inefficient molecular switching. This also suggests that not all molecules in the solution need to be switchable in order to achieve a switchable phase change.

While our predictions have not yet been demonstrated in experiment, it is worth noting that a different kind of molecular switch, based upon photo-induced isomerisation of a fully covalent molecule (with no mechanical bond),³⁰ is used as a dopant to induce chirality in nematic liquid crystals. These

photoswitchable molecules have been shown to provide thermally stable, reversible control³¹ of the structure of cholesteric liquid crystals.

APPENDIX: NUMERICAL APPROACH TO SOLVE EQUATION (4)

Equation (4) cannot be solved analytically and researchers have used different numerical methods to obtain solutions. Here we follow Lekkerkerker's method²³ and expand $\sin \gamma$ in a Legendre series up to order 7, which is sufficiently accurate for our predictions. As explained in Lekkerkerker, symmetry allows us to recast the distribution functions in terms of θ or $\Psi_i(\Omega) \rightarrow \Psi_i(\theta)$ and the Legendre series must be of even order

$$\sin \gamma = \frac{\pi}{4} - \sum_{n=1}^7 d_{2n} P_{2n}(\cos \gamma), \quad (\text{A1})$$

where $d_{2n} = \frac{\pi(4n+1)(2n-3)!!(2n-1)!!}{2^{2n+2}n!(n+1)!}$. Using the addition theorem for spherical harmonics or

$$P_l(\cos \gamma) = P_l(\cos \theta)P_l(\cos \theta') + 2 \sum_{m=1}^l \frac{(l-m)!}{(l+m)!} P_l^m(\cos \theta) \times P_l^m(\cos \theta') \cos [m(\phi - \phi')].$$

Lekkerkerker finds that the orientation distribution functions for the short and long rods are then

$$\begin{aligned} \Psi_s(\theta) &= \frac{\exp[\sum_{n=1}^7 \alpha_{2n} P_{2n}(\cos \theta)]}{N_s}, \\ \Psi_\ell(\theta) &= \frac{\exp[q \sum_{n=1}^7 \alpha_{2n} P_{2n}(\cos \theta)]}{N_\ell}, \end{aligned} \quad (\text{A2})$$

where N_i is a normalisation constant so that $1 = \int d\theta \Psi_i(\theta)$ and α_{2n} is a set of 7 unknown Legendre coefficients. Equation (4) then reduces to a set of 7 equations,

$$\int d\theta [(1-x)\Psi_s(\theta) + xq\Psi_\ell(\theta)]P_{2n}(\cos \theta) = \frac{\pi\alpha_{2n}}{8cd_{2n}} \quad 1 \leq n \leq 7. \quad (\text{A3})$$

Equations (A2) and (A3) provide us with nine equations, which, for a specified concentration, c , and fraction of long rods, x , provide the set of Legendre coefficients or distribution functions Ψ_s and Ψ_ℓ for a solution of rods in a nematic phase. [Recall, in the isotropic phase, $\Psi_s = \Psi_\ell = (4\pi)^{-1}$.]

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