Nematic-nematic demixing in polydisperse thermotropic liquid crystals

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We consider the effects of polydispersity on isotropic-nematic phase equilibria in thermotropic liquid crystals, using a Maier-Saupe theory with factorized interactions. A sufficient spread (≈ 50%) in the interaction strengths of the particles leads to phase separation into two or more nematic phases, which can in addition coexist with an isotropic phase. The isotropic-nematic coexistence region widens dramatically as polydispersity is increased, leading to re-entrant isotropic-nematic phase separation in some regions of the phase diagram. We show that similar phenomena will occur also for non-factorized interactions as long as the interaction strength between any two particle species is lower than the mean of the intra-species interactions.

I. INTRODUCTION

Solutions of anisotropic colloids or stiff polymers can exhibit phase transitions from isotropic to orientationally ordered nematic states as temperature is lowered or density is increased. Such systems are often polydisperse, containing e.g. colloid particles with an effectively continuous range of lengths and diameters or polymers with a distribution of chain lengths. Such polydispersity has experimentally measurable consequences. For example, in polydisperse colloidal rods with nearly hard interactions, demixing into two nematic (N) phases and coexistence of two nematics and an isotropic (I) phase can occur [1, 2]. This is to be contrasted with the hypothesis case where all colloidal particles are identical, i.e. the solution is monodisperse; there at most two phases (I–N) can coexist.

For the theoretical description of phase transitions to nematically ordered states there are two broad classes of models. The first focuses on short-range repulsions between particles and is therefore appropriate for lyotropic liquid crystals whose phase changes are controlled primarily by density. It contains in particular the Onsager model of hard rods, whose second-virial truncation becomes exact in the limit of long thin rods [3], and the Flory lattice model [4]. The second class of models concentrates on the anisotropy of longer-range attractive interactions. It contains in particular the Maier-Saupe model, a mean-field theory which expands the orientational interaction dependence in low-order Legendre polynomials [5, 6]. Models of this type are useful for thermotropics, where temperature is the dominant control parameter. Theories combining these two approaches have also been developed, see the review [7], and extended to include e.g. particle flexibility [8].

For lyotropics, binary (and to lesser extent ternary) mixtures have been thoroughly investigated theoretically using the Onsager and Flory models [9, 10, 11, 12, 13, 14, 15, 16, 17, 18], and phase separation into two nematic (N–N) phases and three-phase I–N–N coexistence predicted for sufficiently disparate rod sizes. Early work on binary thermotropic mixtures ignored the possibility of fractionation, i.e. unequal partitioning of different particle species across coexisting phases. Within this approximation a mixture behaves like a monodisperse system, with no I–N coexistence region [19, 20]. Later studies that accounted for fractionation effects did find I–N and N–N coexistence in bidisperse Maier-Saupe theory. We note as an aside that similar effects have also been seen in theories of mixtures of semi-flexible or stiff polymers; see e.g. [8, 23, 24, 25]. However, there a driving force for demixing even between isotropic phases is normally present, e.g. because of unfavourable interactions between unlike species. N–N demixing then occurs rather trivially when the nematic order prevalent at low temperatures is ‘superimposed’ on this isotropic demixing transition.

Theoretical studies of genuinely polydisperse systems have been rather rarer. For distributions of the polydisperse attribute (particle length, diameter etc) with two narrow peaks one of course expects phase behaviour similar to the bidisperse case [26, 27], but it is not at all obvious what happens for unimodal (single-peaked) distributions. For lyotropics, work on the polydisperse Flory model [28, 29, 30, 31] focussed on general features [32], such as fractionation and the widening of the I–N coexistence region, but did not investigate the possibility of N–N demixing. For the Onsager model, primarily polydispersity in particle lengths has been studied. For a narrow distribution of lengths, perturbative calculations show that the I–N coexistence region again widens [33]. Recent studies [34, 35] for wider length distributions have confirmed this and provided evidence for a region of I–N–N coexistence in the phase diagram. However, the existence of N–N demixing at higher density remains an open question; in simplified Onsager theories N–N coexistence is found only in a limited density range [36, 37] or not at all [38].

For polydisperse thermotropics, Sluckin used Maier-Saupe theory to predict the opening up of an I–N coexistence region in slightly polydisperse systems [39]. This was based on a perturbation theory around the monodisperse case, which did not allow for a study of possible N–N demixing. Semenov obtained similar results for ther-
motropic semi-flexible polymers with small polydispersity in the chain lengths [10].

Our aim in this paper is to find out whether a unimodal distribution of the polydisperse attribute is enough to cause N–N demixing and the associated I–N–N coexistence in polydisperse thermotropics. We use the simplest Maier-Saupe theory for this purpose, with factorized interactions. As explained in the next section, this gives a truncatable free energy for which phase equilibria can be calculated relatively efficiently. The resulting phase diagrams are presented in Sec. III and wider implications and possible generalizations are discussed in Sec. IV.

II. METHOD

We consider a system with liquid crystal particles having a continuous range of values of some polydisperse attribute $l$. This could be particle length, for example, or polarizability in the case of van der Waals interactions; for definiteness we refer to length below. The state of a single phase of a system is then described by a distribution $n(l,\Omega)$, defined so that $n(l,\Omega)\,dl\,d\Omega/4\pi$ gives the fraction of particles with length in an interval $dl$ around $l$, and orientations $\Omega$ in a solid angle $d\Omega$. This distribution is the natural extension for a polydisperse system of the usual orientational distribution $P(\Omega)$ used for monodisperse systems of rods [11]. The rod orientation $\Omega$ can be parameterized in terms of the angle $\theta$ with the nematic axis and an azimuthal angle $\varphi$; due to the cylindrical symmetry of the nematic phase $n(l,\Omega)$ is independent of $\varphi$. Using $d\Omega = d\cos\theta \,d\varphi$ the length distribution, obtained by integrating over orientations, is therefore

$$n(l) = \frac{1}{4\pi} \int d\Omega \,\rho(l,\Omega) = \int d\theta \, n(l,\theta)$$ (1)

where $\int d\theta \ldots = (1/2) \int_0^1 dl \,d\cos\theta \ldots$. The orientational distribution of the particles can be factored out from $n(l,\theta)$ as [38]

$$n(l,\theta) = n(l)P_l(\theta)$$ (2)

where $P_l(\theta)$ represents the probability of finding a rod of given length $l$ in orientation $\Omega = (\theta,\varphi)$ and is normalized according to $\int d\theta \,P_l(\theta) = 1$. In the isotropic phase, one has $P_l(\theta) \equiv 1$ and $n(l,\theta) = n(l)$.

In the above notation the free energy per particle of polydisperse Maier-Saupe theory [38] can be written as $f = f_{\text{id}} + f_{\text{ex}}$, where the ideal part $f_{\text{id}}$ is the free energy of an ideal mixture while the excess part is

$$f_{\text{ex}} = -\frac{1}{2} \int dl \,dl' \,n(l)n(l')u(l,l')S(l)S(l')$$ (3)

Here $S(l) = \int d\theta \,P_l(\theta)P_2(\cos\theta)$ is the orientational order parameter of particles with length $l$, defined as the average of the second Legendre polynomial $P_2(\cos\theta) = \frac{1}{2}(3\cos^2\theta - 1)$. The coefficients $u(l,l')$ determine the strength of the attractive interaction favouring nematic ordering and depend on the particle lengths $l$ and $l'$. We note that the description of the system in terms of a normalized distribution over lengths and orientations rather than a density distribution contains the implicit assumption that density variations with temperature or between coexisting phases are weak and can be neglected. Accordingly, we will not concern ourselves with the density dependence of the interaction strengths $u(l,l')$. Maier and Saupe [4] assumed this to be quadratic, but Cotter [2] later showed that a thermodynamically consistent derivation of Maier-Saupe theory as a mean-field approximation requires a linear density scaling.

In the following we make the common assumption that the interaction strengths factorize according to $u(l,l') = [u(l,l)u(l',l')]^{1/2}$. It is then sensible to switch from $l$ to $u \equiv u(l,l)$ as the polydisperse attribute, giving for the ideal and excess free energies ($k_B = 1$)

$$f_{\text{id}} = T \int du \,\tilde{u}\,n(u,\theta) \ln n(u,\theta)$$ (4)

$$= T \int du \,n(u) \left[ \ln n(u) + \int d\theta \,\tilde{u} \,P_u(\theta) \ln P_u(\theta) \right]$$ (5)

$$f_{\text{ex}} = -\frac{1}{2} \int du \,u \,n(u)n(u') \sqrt{\tilde{u}} \,n(\theta)S(\theta)S(\theta')$$ (6)

With our factorized interactions the underlying nature of the polydisperse attribute has become irrelevant; polydispersity manifests itself only through the spread in the interaction strengths $u$.

For a given distribution $n(u)$, the orientational distributions are obtained by minimization of the free energy with respect to the orientational distributions $P_u(\theta)$. Bearing in mind that these are normalized, one finds

$$P_u(\theta) = z^{-1}(u) \exp \left( \beta S \sqrt{u} \,P_2 \right)$$ (7)

$$z(u) = \int d\theta \,\exp(\beta S \sqrt{u} \,P_2)$$ (8)

where we have abbreviated $\beta = 1/T$ and $P_2 \equiv P_2(\cos\theta)$ and $z(u)$ is the normalizing partition function for $P_u(\theta)$. The order parameter that appears in [15] is

$$\bar{S} = \int du \,n(u)\sqrt{u}S(u) = \int du \,\tilde{u} \,n(u,\theta)\sqrt{u} \,P_2$$ (9)

and determines the excess free energy $f_{\text{ex}} = -\bar{S}^2/2$. It obeys the self-consistency equation

$$\bar{S} = \int du \,\tilde{u} \,n(u)\sqrt{u} \,P_2 \exp \left( \beta S \sqrt{u} \,P_2 \right)$$ (10)

This always has the trivial solution $\bar{S} = 0$ corresponding to an isotropic phase; nematic phases are characterized by $\bar{S} > 0$ and become physically relevant where they have a lower free energy than the isotropic solution.

To calculate phase equilibria we need the chemical potentials $\mu(u)$, which need to be equal in coexisting
phases. Denote $N(u)$ the particle number distribution, so that the total particle number is $N = \int du \, N(u)$, and $n(u) = N(u)/N$. Then $\mu(u) = \delta F/\delta N(u)$, where the extensive free energy is $F = NF[N(u)/N]$. This gives

$$\mu(u) = \frac{\delta f}{\delta n(u)} + f - \int du' n(u') \frac{\delta f}{\delta n(u')} \tag{11}$$

In evaluating the derivatives $\delta f/\delta n(u)$ we do not need to take into account the variation of the $P_u(\theta)$ because they are chosen to minimize $f$. A short calculation then gives $\delta f/\delta n(u) = T \ln(n(u)/z(u)) + T$ and so

$$\mu(u) = T \ln \frac{n(u)}{z(u)} + \frac{1}{2} S^2 \tag{12}$$

If the system separates into $P$ phases $a = 1, \ldots, P$, their $u$-distributions $n_a(u)$ can therefore be written as

$$n_a(u) = R(u)z_a(u) \exp(-\beta S^2_a/2) \tag{13}$$

The common factor $R(u) = \exp(\beta \mu(u))$ follows from the requirement of particle conservation: if phase $a$ contains a fraction $x_a$ of all particles, then $\sum_a x_a n_a(u) = n_0(u)$, where $n_0(u)$ is the overall or “parent” distribution of $u$. Using also \(7\), the joint distribution over interaction strengths and orientations in each phase therefore takes the form

$$n_a(u, \theta) = \frac{n_0(u) \exp(\beta S_a \sqrt{u} P_2 - \beta S^2_a/2)}{\sum_b x_b \int d\theta \exp(\beta S_b \sqrt{u} P_2 - \beta S^2_b/2)} \tag{14}$$

A phase split involving $P$ phases is therefore characterized by the $2P$ variables $S_a$ and $x_a$. These are determined by as many conditions, namely

$$1 = \int du \, d\theta \, n_a(u, \theta) \tag{15}$$

$$\bar{S}_a = \int du \, d\theta \, n_a(u, \theta) \sqrt{u} P_2 \tag{16}$$

The relations \(15\) automatically guarantee that $\sum_a x_a = 1$ because the parent $n_0(u)$ is normalized by assumption.

In our numerical work, we exploit the fact that the excess free energy $f_{\text{ex}} = -S^2/2$ is truncatable \(12\), i.e. it involves only a single moment $\bar{S}$ of the distribution $n(u, \theta)$. Phase equilibria can then efficiently be found using the method \(13\). This constructs a MFE which depends only on $\bar{S}$, and from which phase coexistence can be predicted in the standard manner. In this simplest form the MFE gives only the onset of phase separation exactly. However, by including additional moments, defined by adaptively chosen weight functions, increasingly accurate solutions are obtained. Using these as initial points, we are then able to find the, for our free energy, exact solutions of the phase equilibrium equations \(13\), \(14\), \(15\). We omit the details of the implementation because they are similar to our study of an approximate Onsager model \(16\). Differences arise primarily because, in the Maier-Saupe model, we are describing the system in terms of normalized distributions, as would be appropriate in other systems for the case of fixed pressure rather than fixed volume; the appropriate modifications of the MFE approach are described in \(12\).

III. RESULTS

We concentrate on the example case of a Schulz parent distribution of interaction strengths, given by

$$n_0(u) \propto u^z e^{-(z+1)u} \tag{17}$$

The coefficient in the exponent has been chosen such that the mean interaction strength $\langle u \rangle_0$ is fixed to unity, thus setting our energy and temperature scale. The width of the distribution is characterized by its standard deviation divided by its mean. This quantity, denoted $\delta$ below, is often also referred to simply as the polydispersity and is related to $z$ by $\delta = (1 + z)^{-1/2}$. To avoid interaction strengths which are arbitrarily large compared to the mean, we impose an upper cutoff of $u_{\text{max}} = 4$. This affects the mean value of $u$ only negligibly in the range of $\delta$ of interest to us, while the relation between $\delta$ and $z$ has to be calculated numerically.

Fig. 1 shows the resulting phase diagram, indicating for each given parent polydispersity $\delta$ (in the range $\delta = 0\ldots0.60$) and temperature the nature of the phases coexisting at equilibrium. Figuring first on the inset, which shows the whole range of $\delta$, we see that in the monodisperse limit $\delta \to 0$ there is no coexistence gap,
with the transition from the isotropic (I) to the nematic (N) phase taking place at the well-known Maier-Saupe temperature of $1/T_c \approx 4.54$. At nonzero $\delta$ an I–N coexistence region appears. Its width initially grows quadratically with $\delta$, as predicted by perturbation theory for small $\delta$. However, as $\delta$ increases, the two boundaries of this I–N region are affected in an increasingly asymmetric way. The onset temperature of nematic ordering comes from high $T$ changes rather little, increasing by only around 12% as the polydispersity increases from zero to $\delta = 0.6$. The lower boundary of the I–N region, on the other hand, is shifted to significantly lower temperatures. In fact the broadening is so strong that the phase boundary becomes re-entrant: for $0.553 < \delta < 0.567$ one has the phase split sequence $I \rightarrow I\rightarrow N \rightarrow I\rightarrow N \rightarrow \ldots$ as temperature is lowered.

For polydispersities above $\delta \approx 0.45$, Fig. 2 shows in addition that the system can fractionate from a single-phase nematic into two and later even three coexisting nematics as $T$ is lowered. The boundary of the N–N region meets that of the I–N region, and at that point a three-phase coexistence region (I–N–N) opens up where one isotropic and two fractionated nematic phases coexist. The structure of the phase diagram in this area is similar to the high-density phase diagram of polydisperse hard spheres, where two or more fractionated solids can occur with our without a coexisting fluid phase.

It is worth emphasizing that all coexistence regions in the phase diagram are caused by polydispersity; the monodisperse system only has an I–N transition at a single temperature. Also, the presence of an effectively infinite number of different particle species, characterized by their respective interaction strengths $u$, means that the number of possible phases can be in principle arbitrary. This should be contrasted with the case of a binary mixture, which is illustrated in Fig. 2 for particles with interaction strengths $u_1 = 1$ and $u_2 = 3.5$; $x$ is the fraction of particles of the second kind in the parent. A region of N–N demixing again occurs at low temperatures, but I–N–N coexistence is possible only at a single temperature.

The rich phase behaviour that occurs in the polydisperse system is driven by fractionation, i.e. by the fact that particles of different interaction strength $u$ partition themselves unevenly among coexisting phases. As an example, we show in Fig. 3 the distributions $n_a(u)$ for the three coexisting phases (I–N–N) into which a Schulz parent with $\delta = 0.571$ splits at $1/T = 15$ (compare Fig. 1). The more weakly interacting particles are found predominantly in the isotropic phase, while the particles with larger $u$ are partitioned across the two nematic phases. This tendency is observed more generally, as the case of two-phase I–N coexistence in the inset of Fig. 3 shows. Physically, it is explained easily from the form of the Maier-Saupe free energy: the system can lower its excess free energy (only) by ordering nematicallly. This effect is stronger for the more strongly interacting particles, which are therefore found preferentially in the nematic phases.

As a consequence of fractionation, the overall particle number fractions $x_a$ found in the various coexisting phases also do not vary linearly across coexistence region. Fig. 4 illustrates this, for a Schulz parent with the same polydispersity $\delta = 0.571$ as in the two examples in Fig. 3. One notes in particular the non-monotonic variation of the fraction of particles in the isotropic phase before the second nematic phase appears. This is due to the proximity to the re-entrant I–N phase boundary in the phase

FIG. 2: Phase diagram for a bidisperse mixture with interaction strengths $u_1 = 1$ and $u_2 = 3.5$; $x$ is the fraction of particles of the second kind in the parent. The dashed line indicates the temperature where three phases (I–N–N) can coexist.

FIG. 3: Distributions of particles according to interaction strength, $n_a(u)$. The solid lines show the three coexisting phases (I–N–N) at $\delta = 0.571$ and $1/T = 15$; the dashed line is the parent distribution. Inset: Same for the I–N coexistence at $\delta = 0.571$ and $1/T = 5.5$. 

FIG. 1: Illustration of the distribution of particles in a Schulz parent with $\delta = 0.5$; the dashed line is the parent distribution. Inset: Same for the I–N coexistence at $\delta = 0.5$ and $1/T = 5.5$. 

FIG. 4: Distributions of particles according to interaction strength, $n_a(u)$ for the three coexisting phases (I–N–N) into which a Schulz parent with $\delta = 0.571$ splits at $1/T = 15$ (compare Fig. 1).
FIG. 4: Volume fractions $x_n$ of the various coexisting phases plotted as a function of inverse temperature, for a Schulz parent with polydispersity $\delta = 0.571$.

IV. DISCUSSION

We have studied the effect of polydispersity in thermotropic liquid crystals, using a Maier-Saupe theory with factorized interactions. For a spread of interaction strengths $u$ of around $\delta = 0.50$ of the mean and higher, polydispersity causes new phase splits to appear in the phase diagram. In particular, the theory predicts coexistence of two or more nematics with or without an additional isotropic phase. Together with this, a strong broadening of the I–N coexistence region is observed, to the extent that the phase boundary between the N and I–N regions becomes re-entrant within a small range of $\delta$. Our calculation only considered isotropic and nematic phases and so at least some of phase behaviour we found at lower $T$ will be only metastable, the stable phases being e.g. smectic or crystalline. Nevertheless, one would expect to be able to observe at least the strong widening of the I–N coexistence region in appropriate experimental systems.

From a broader theoretical point of view, our results demonstrate that polydispersity in the attractive (and orientation-dependent) interaction between liquid crystal particles can be sufficient to cause demixing into two or more nematic phases. Polydispersity in short-range repulsions as caused e.g. by a distribution of particle shapes is not necessary, although from the results for binary mixtures in the Onsager model one would expect it to reinforce the tendency towards nematic demixing. This issue would merit further study but promises to be very challenging. Indeed, even in the polydisperse Onsager model without added attractive interactions it remains an open problem to establish the existence of nematic-nematic demixing at high densities.

One may ask how crucial the assumption of factorized interactions $u(l, l') = u^{1/2}(l, l)u^{1/2}(l', l')$ is for the phase behaviour that we have found. The situation is easiest to understand at low temperatures, where one has full nematic order ($S(l) \approx 0$) and the ideal (entropic) part of the free energy can be neglected. The system then has to minimize the excess free energy $-\frac{1}{2} \int dl dl' n(l)n(l')u(l, l')$. To understand whether phase separation will occur, take first the simple case of a binary mixture, with a fraction $x$ of particles of length (polarizability, etc) $l$ and fraction $(1-x)$ of particles of length $l'$. The demixed state of two phases, each containing only one type of particles, has a lower free energy than the mixed phase if

$$-\frac{1}{2} [lx(l, l) + (1-x)u(l', l')] < -\frac{1}{2} [x^2 u(l, l)]$$

$$+ (1-x)^2 u(l', l') + 2x(1-x)u(l, l')]$$

or equivalently

$$u(l, l') < \frac{1}{2} [u(l, l) + u(l', l')]$$

One can easily show that this condition in fact guarantees that any mixture of a finite number of components will separate into phases each containing only one component. In a fully polydisperse system, one then effects a cascade of demixing transitions with an ever-increasing number of phases as $T$ is lowered, as is found in e.g. models of polydisperse copolymer blends [15]. Our observation of demixing into multiple nematic phases should therefore be generic as long as $\delta$ holds, i.e. as long as the attractive interaction strength between different particle species is always lower than the mean of the intra-species interaction strengths.

In future work, one could contemplate extending the present study by accounting for the effects of density variations. To a first approximation this can be done by dividing the interaction strengths $u(l, l')$ by the average particle volume in the given phase [21]. In the polydisperse setting, this would give an extra factor of $1/\bar{v}$ in the excess free energy, where $\bar{v} = \int dl n(l)v(l)$ and $v(l)$ is the particle volume as a function of $l$. One then still has a truncatable free energy, but now with an excess part depending on two moments, $\bar{S}$ and $\bar{v}$. Also of interest would be an extension to liquid crystal polymers, where perturbative results for small polydispersity $\delta$ already exist [40], and there is experimental evidence for N–N phase separation, at least in binary mixtures [43].

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