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Stabilization of a blue phase by a guest component: An approach based on a Landau–de Gennes theory

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We discuss, with the aid of numerical calculations based on a Landau–de Gennes theory, the stabilization of a blue phase in chiral liquid crystals by introducing a guest component. Our argument is based on a common speculation that cores of disclination lines with higher free-energy density are replaced by the guest component. We assume that the guest component forms sharp interfaces with the liquid crystal (strong segregation). We show that, by a suitable choice of materials with small interfacial tension, a guest component of volume fraction less than 10% drastically increases the temperature range of thermodynamic stability of a blue phase, in agreement with experiments [Kikuchi *et al.*, Nature Mater. **1**, 64 (2002)].

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I. INTRODUCTION

Blue phases (BPs) [1,2] have been known as peculiar mesophases of highly chiral liquid crystals with distinct Bragg reflection in the visible wavelength range together with optical isotropy. They appear as thermodynamically stable phases in the temperature range between an isotropic phase (Iso) and a cholesteric (or chiral nematic) phase with helical order (N^*). The origin of these optical properties was thoroughly investigated, and now it is well established that BPs are made up of a three-dimensional stack of double-twist cylinders and topological line defects called disclinations. In Fig. 1(a), we show the disclination arrangement of one blue phase referred to as BP I with the symmetry of $O_8[I4_132]$. Figure 1(b) illustrates the orientation profile of a double-twist cylinder. Blue phases have thus attracted interest as an intriguing example of systems containing topological defects not only in the field of liquid crystals; blue phases have been argued as possible ordered structures in chiral ferromagnets such as MnSi [3]. We notice also that double-twist orientational order is a typical example of topological excitations referred to as skyrmions, which have been found in various systems such as spinor Bose-Einstein condensates [4] and electrons confined in two dimensions [5].

The occurrence of these complex orientational structures stems from a competition between local preference of a double-twist structure over a single twist of N^* phase and the energetic cost of disclination lines inevitable from topological requirement. Possibly due to the delicate balance of these two ingredients, the temperature range of the thermodynamic stability of BPs is in most cases ~1 K or less. This was a serious drawback of BPs for practical applications, though the coexistence of fluidity and three-dimensional order, together with their fascinating optical properties, is highly appealing.

Recently, however, BPs with wider temperature range were reported by several groups [6–8]. Among them, Kikuchi and co-workers reported a promising technique of introducing photo-cross-linked polymers as a guest component in the BP matrix. They showed that the temperature range of the stability can be over 60 K [6] and that the orientational order in their BPs is not fixed by the guest polymer, which results in a fast electro-optical switching. BPs with wider temperature range of stability retaining fluidity opened up a possibility of their use in practical applications. One interesting example is mirrorless lasing [9,10], and a release of a prototype fast-switching display using BPs [11] impacted the field of liquid crystal displays.

Though several theoretical studies have been carried out on the stability of BPs of pure liquid crystals [1,12–16], the only theoretical argument on the stabilization of BPs by mixing liquid crystals with other components was given by Huang *et al.* [17]. They studied the effect of emulsification but did not discuss quantitatively the composition dependence on the temperature range of stabilized BPs. In the present study, we give a theoretical argument on the contribution of the guest component to the thermodynamic stabilization of BPs. Our argument is based on the common speculation [6] that the replacement of the disclination core regions with high free-energy density [depicted in Fig. 1(a)] by a guest component can reduce the total free energy of BPs, thus stabilizing BPs over N^* phase. Note that a recent experiment gave evidence of the aggregation of the guest component (photo-cross-linked polymers) at the lattice of disclinations [18]. Nevertheless, so far as we know, no theoretical discussion has been made as to whether this speculation really gives a proper account for the stabilization of BPs. We will check its validity and show that the introduction of a guest component with the volume fraction of 10% or less can stabilize BPs substantially.

II. THEORETICAL ARGUMENT

Our first assumption is that the liquid crystal and the guest component segregate strongly. The region occupied by the liquid crystal and that by the guest component are then separated by a sharp interface. One case in which this assumption is justified is that the mixing of these two components is energetically disfavored. Another such case is that the guest

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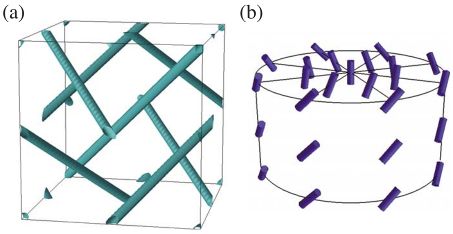

FIG. 1. (Color online) (a) Disclination profile of BP I in a cubic unit cell. Here we show the results of our numerical calculation with the temperature $\tau=-5$. The regions with the rescaled free-energy density f/f_0 larger than -10.50 are depicted. The largest and smallest values of f/f_0 in the system are -6.51 and -11.94, respectively. See text for the definitions of variables τ and f/f_0. (b) Schematic illustration of a double-twist cylinder. The director shows twist in all directions perpendicular to the vertical cylinder axis, in contrast to the N^* phase whose twist is only along one direction (single twist).

component is a polymer with high molecular weight; the mixing entropy becomes unimportant [19]. The latter case corresponds to the work of Kikuchi *et al.* [6] who used photo-cross-linked polymers for the stabilization of blue phases.

The next assumption is that the guest component can replace the disclination core regions with higher free-energy density without disturbing the orientation profile of the host liquid crystal. Then the anchoring at the interface between the liquid crystal must be weak enough. Moreover, the interfacial free energy cannot be large; otherwise, the shape of the region occupied by the guest component should be determined by the balance between the energy gain by the replacement and the interfacial free energy. The validity of these postulations will be discussed later. Once they are justified, for the determination of the orientation profile of a blue phase with a guest component, we only have to calculate the profile of a pure liquid crystal without a guest component and determine the regions with higher free-energy density that will be replaced by the guest component.

A. Landau–de Gennes theory

Our theoretical argument on the BP is based on a Landau–de Gennes theory, in which the orientational order is described by a second-rank symmetric and traceless tensor $Q_{\alpha\beta}$. We follow the notation in Ref. [1] and write the free-energy density as

$$f\{\mathsf{Q}\} = c\,\mathrm{Tr}\,\mathsf{Q}^2 - \sqrt{6}b\,\mathrm{Tr}\,\mathsf{Q}^3 + a(\mathrm{Tr}\,\mathsf{Q}^2)^2 + \frac{1}{4}K_1[(\nabla\times\mathsf{Q})_{\alpha\beta} + 2q_0Q_{\alpha\beta}]^2 + \frac{1}{4}K_0[(\nabla\cdot\mathsf{Q})_\alpha]^2. \quad (1)$$

The first three terms with material parameters a, b, and c represent local free energy as a Landau expansion and the last two terms with elastic constants K_0 and K_1 take care of the spatial variation of the orientational order. The pitch of a cholesteric helix is $2\pi/|q_0|$, and hereafter we choose $q_0>0$. After an appropriate rescaling of the variables, f can be rewritten as

$$f\{\chi\}/f_0 = \tau\,\mathrm{Tr}\,\chi^2 - \sqrt{6}\mathrm{Tr}\,\chi^3 + (\mathrm{Tr}\,\chi^2)^2 + \kappa^2\{[(\tilde{\nabla}\times\chi)_{\alpha\beta} + \chi_{\alpha\beta}]^2 + \eta[(\tilde{\nabla}\cdot\chi)_\alpha]^2\}, \quad (2)$$

where we have introduced a rescaled order parameter $\chi \equiv (a/b)\mathsf{Q}$, a rescaled spatial derivative $\tilde{\nabla}\equiv(2q_0)^{-1}\nabla$, and the unit of free-energy density $f_0\equiv b^4/a^3$. Here, $\kappa\equiv\sqrt{aK_1q_0^2/b^2}$ measures the strength of chirality, and we choose $\kappa=0.4$. As typical values of material parameters, we have $a\simeq 8\times10^4$ J m^{-3}, $b\simeq5\times10^4$ J m^{-3} [20,21], and $K_1\simeq10$ pN [1]. Our choice of κ thus corresponds to the cholesteric pitch $2\pi/q_0\simeq300$ nm in the range of its typical values of liquid crystals showing BPs [1]. The parameter $\eta\equiv K_0/K_1$ concerns the anisotropy of elasticity, and we set $\eta=1$ (the so-called one-constant approximation). The rescaled temperature is given by $\tau\equiv(a/b^2)c$. In the usual Landau theory, the temperature dependence of c plays a dominant role in phase transitions. Linear dependence of c is assumed so that it is expressed as $c=\tilde{c}(T-T^*)$, where T is the absolute temperature in kelvin and T^* is the temperature at which the isotropic state $Q_{\alpha\beta}=0$ becomes unstable. From a typical value $\tilde{c}\simeq3\times10^4$ J m^{-3} K^{-1} [20,21], we have $\tau\simeq1\times(T-T^*)$. Though the original Landau theory for superconductivity or critical phenomena and the Landau–de Gennes theory are, in principle, applicable only around the critical or the transition point, we use the Landau–de Gennes theory in a wider temperature range as one of the few quantitative theories available for the thermodynamic behavior of liquid crystals.

B. Calculation of the orientation profile

We calculate the profile of the BP (without the guest component) by solving the Euler-Lagrange equation,

$$\frac{\delta F}{\delta\chi_{\alpha\beta}(\boldsymbol{r})} - \lambda\delta_{ij} = 0, \quad (3)$$

where λ is a Lagrange multiplier ensuring the tracelessness of $\chi_{\alpha\beta}$ and $F=\int_{\Omega_{\mathrm{tot}}}d\boldsymbol{r}f\{\chi\}$ is the total free energy. We use the numerical scheme developed in Ref. [22], in which not only the order parameter χ but also the lattice spacings are relaxed in the course of calculation. The total volume of the calculation Ω_{tot} is set on an N^3 cubic lattice with $N=64$ on which periodic boundary conditions are imposed.

For $\kappa=0.4$, BP I is the most stable phase in the range $-0.610\lesssim\tau\lesssim0.233$; at lower and higher temperatures the most stable phases are N^* and Iso, respectively. We find no thermodynamically stable BP II with $O_2(P4_232)$ symmetry for $\kappa=0.4$. In the present study we focus the thermodynamic stability of BP I over N^* at lower τ and do not discuss BP II. Note also that the thermodynamic stability of BP I over Iso at higher temperatures is not significantly affected by the guest component [23], which was indeed observed by Kikuchi *et al.* [6].

C. Free energy of blue phases with a guest component

After calculating the profile of BP I for a given temperature τ, the free-energy density profile $f(\boldsymbol{r})$ or f_i can be obtained from the calculated order-parameter profile. (Here the index $i=1,2,\ldots,N^3$ labels the numerical lattice points.) Next we sort the set $\{f_i\}$ so that f_i becomes a monotonically decreasing function of i. Then, by choosing the lattice points with $i\leq\phi N^3$, one can determine the region of volume fraction ϕ with higher f that must be replaced by the guest component of the same volume fraction. The volume fraction ϕ of regions with higher f depicted in Fig. 1(a) ($f/f_0 > -10.50$) is 0.0156.

We denote the region replaced by the guest component by $\Omega_{\rm c}$. The total free energy of a BP with a guest component is then written as

$$F_{\rm BP}=\int_{\Omega_{\rm tot}-\Omega_{\rm c}} d\boldsymbol{r}f(\boldsymbol{r})+\Omega_{\rm tot}(\phi f_{\rm g}+\sigma s), \tag{4}$$

where $f_{\rm g}$ is the free-energy density of the guest component assumed to be independent of position. The last term describes the contribution of the interfaces between the liquid crystal and the guest component which we will discuss below; σ is the interfacial energy and s is the area of the interface per unit volume. To check the stability of the BP with a guest component, we have to compare $F_{\rm BP}$ with the total free energy of N^* phase with the same amount of the guest component. The latter is given by

$$F_{N^*}=\Omega_{\rm tot}\{(1-\phi)f_{N^*}+\phi f_{\rm g}\}, \tag{5}$$

where f_{N^*} is the free-energy density of the N^* phase that is again position independent. It is expected that in the N^* phase, the guest component will phase separate macroscopically, in which case s becomes zero in the thermodynamic limit. From Eqs. (4) and (5), the free-energy difference per unit volume is given by

$$F_{\rm BP}-F_{N^*}=\int_{\Omega_{\rm tot}-\Omega_{\rm c}} d\boldsymbol{r}f(\boldsymbol{r})+\Omega_{\rm tot}\{-(1-\phi)f_{N^*}+\sigma s\}. \tag{6}$$

D. Contribution of the interfacial free energy

Here we discuss the contribution of the interface between the liquid crystal and the guest component. Let l be the dimension of the unit cell of BP I. We postulate that the guest component occupies cylindrical regions of radius r whose axes are identical to disclination lines. As long as ϕ is small enough, this postulation is reasonable from the appearance of disclination core regions shown in Fig. 1(a).

From the profile in Fig. 1(a), one can also see that a unit cell of BP I contains disclination lines corresponding to four diagonals. Therefore, the length of disclination lines per unit cell of BP I is $4\sqrt{3}l$. The area of the interfaces per unit volume is

$$s=\frac{(4\sqrt{3}l)\cdot 2\pi r}{l^3}=\frac{8\sqrt{3}\pi r}{l^2}. \tag{7}$$

The volume of the cylindrical regions is $4\sqrt{3}l\cdot\pi r^2$, which is equal to that occupied by the guest component, ϕl^3. Thus, we have

$$r=l\sqrt{\frac{\phi}{4\sqrt{3}\pi}}. \tag{8}$$

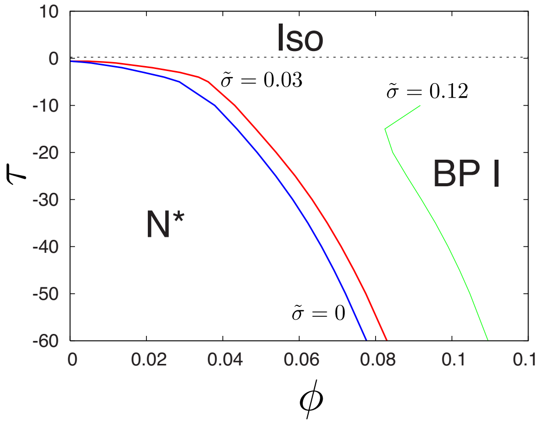

FIG. 2. (Color online) Phase diagram of the BP with a guest component of volume fraction ϕ. For reference, the boundary between BP I and Iso ($\tau\simeq 0.233$) is also shown as a dotted line. Note that $\tau\simeq 1\times(T-T^*)$, where the temperatures T and T^* (at which isotropic phase loses its stability) are in kelvin.

The rescaled contribution of the interfacial energy is

$$\frac{\sigma s}{f_0}=\tilde{\sigma}\sqrt{\phi}, \tag{9}$$

where, using Eqs. (7) and (8), we have defined a dimensionless variable

$$\tilde{\sigma}\equiv\frac{4(\sqrt{3}\pi)^{1/2}\sigma}{f_0 l}\simeq 3\times 10^3\sigma. \tag{10}$$

Here σ is in units of J m^{-2} and we have used $l\simeq 2\pi/q_0 \simeq 300$ nm. The value of σ in actual systems is unavailable in practice, but in several previous theoretical studies on the stability of blue phases (without guest components) [13,17], the upper bound of the energy of the interface separating the core region in the liquid crystal is estimated to be around 10^{-5} J m^{-2}. We therefore expect that for the stability of BPs, σ cannot be too larger than 10^{-5} J m^{-2}. We also notice that the surface anchoring energy W is on the order of or smaller than σ. Hence, $Wr/K_1 \ll 1$, which indicates that the surface anchoring is not important compared with the elasticity of the liquid crystal. This argument justifies our implicit assumption that the surfaces do not distort the orientational profile of the liquid crystal.

III. RESULTS

The free-energy difference $F_{\rm BP}-F_{N^*}$ given by Eq. (6) depends on ϕ and τ, and the boundary between BP I and N^* in the (ϕ,τ) phase diagram can be determined by solving $F_{\rm BP}-F_{N^*}=0$. In Fig. 2, we plot the phase diagram for different interfacial energy, $\tilde{\sigma}=0$, 0.03 ($\sigma\simeq 1\times 10^{-5}$ J m^{-2}), and 0.12 ($\sigma\simeq 4\times 10^{-5}$ J m^{-2}).

What we want to stress here is that for $\tilde{\sigma}=0$ and 0.03, the temperature range of the stability of BP I becomes significantly wider with the increase of ϕ. Recalling $\tau \simeq 1 \times (T-T^{*})$, we find that the temperature range of stable BP I can be larger than 60 K by introducing a guest component of volume fraction less than 10%. Kikuchi *et al.* [6] found that by photo-cross-linked polymers of around 6 wt % increase the temperature range of stable BP I to larger than 60 K. Since in organic materials the weight percent and the volume fraction in percent do not differ significantly, our results are in semiquantitative agreement with experimental findings and can thus explain how large the stability range of BP I can be and how much guest component is necessary for achieving it. Notice also that the interfacial energy on the order of 1×10^{-5} J m^{-2} yields only a small quantitative change in the stability of BP I.

We have shown the results for $\tilde{\sigma}=0.12$ to clarify the limitation of our theoretical argument; the phase boundary cannot be determined for small $|\tau|$. It is because for small $|\tau|$ the free-energy gain due to the replacement of the defect core region is too small to overcome the free-energy loss by interfaces when σ is large enough. We speculate that our argument above needs some modifications. Indeed, when the interfacial free energy is large enough, a thin cylindrical region is energetically costly and would be broken into a number of spherical droplets to reduce the interfacial area.

From the results shown above, we have to choose suitable materials whose interfacial energy with the host liquid crystal is around 1×10^{-5} J m^{-2} or smaller, though precise determination of the interfacial energy in the length scale of a few hundreds of nanometers is an experimental challenge.

IV. CONCLUSION

In conclusion, we have discussed the origin of the stabilization of blue phases by a guest component. Using numerical calculations based on a Landau–de Gennes theory, we have checked the validity of the common speculation that stabilization is brought about by the replacement of energetically costly disclination core regions by the guest component. We have shown that, by a suitable choice of materials immiscible with liquid crystals and whose interfacial energy is on the order of 1×10^{-5} J m^{-2} or smaller, the introduction of the guest component of volume fraction less than 10% can significantly increase the stability range of blue phases from $\sim$1 K to a few tens of kelvin or even larger. Our results are in good agreement with previous experiments using photo-cross-linked polymers as a guest component, which is surprising when we recall the assumptions and simplifications employed in our argument. Considering the absence of a theoretical argument on this problem so far, we believe that we have given a convincing theoretical basis on the understanding of the stabilization blue phases by introducing a guest component.

We also notice that recently there has been growing interest in the possibility of increasing the stability of blue phases by nanoparticles [24–26]. The mechanism of the stabilization of blue phases by nanoparticles is believed to be similar to what we have discussed here, and indeed, a simulation study has demonstrated that nanoparticles are attracted by disclination lines [24]. Thus, our argument could be useful for an appropriate choice of nanoparticles with smaller surface energy. We further notice that in soft materials there exist other thermodynamically stable phases containing an array of defects. One typical example is a twist grain-boundary-phase found in chiral smectic liquid crystals [27]. They have regular periodic structures in many cases and, if stabilized, could be used for interesting photonic applications. We hope that our theoretical argument, though simple enough, could be applied for seeking the possibility of stabilizing such defect phases other than blue phases.

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