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Notes

Pitch Contributions to the Cholesteric−Isotropic Interfacial Tension

Alejandro D. Rey*

Department of Chemical Engineering, McGill University, 3610 University Street, Montreal, Quebec, Canada H3A 2B2

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Phase transitions in lyotropic and thermotropic liquid crystalline systems are a topic of current fundamental and applied research.[1] An important feature that impinges on the kinetic, thermodynamic, and morphological properties of biphasic systems involving order/disorder phases is the interfacial tension. The interfacial tension at the nematic−isotropic (N/I) phase transition has been studied extensively theoretically[2−6] and experimentally,[7,8] and its basic features are sufficiently well understood. On the other hand, the interfacial tension of the cholesteric−isotropic (Ch/I) interface has been experimentally characterized,[9] and as already pointed out by de Gennes and Prost,[10] it is difficult to analyze. One of the reasons is that cholesteric liquid crystals are layered materials that behave as nematic liquid crystals at length scales smaller than the layer spacing and as smectic liquid crystals at length scales longer than the layer spacing. A further complication is that the layer spacing, known as the pitch of the cholesteric helix, is a function of pressure, temperature, concentration, and the nematic scalar order parameter.[10,11,14] Since the pitch is a function of the scalar order parameter, at the cholesteric/isotropic interface, the gradients in the scalar order parameter lead to gradients in the pitch. It is then clear that the interfacial tension between isotropic−cholesteric phases contains additional contributions not found in the nematic−isotropic interface, because nematics are positionally disordered materials while cholesteric are layered materials. Thus, a better understanding of layer spacing contributions to the interfacial tension is highly desirable.

Recently the interfacial tension between the Ch/I interface was carefully studied theoretically and experimentally,[9] and it was found that several theories[2−4] that describe the N/I interface predict the correct molecular weight dependence of the interfacial tension but underpredict its magnitude. In addition, the experiments[9] clearly show pitch gradients in the direction normal to the interface, in agreement with the experimentally obeserved[14] and theoretically expected[14] pitch dependence on the scalar order parameter.

The objective of this note is (i) to use the uniaxial version of Landau−de Gennes theory[12] to characterize the interfacial tension of the cholesteric−isotropic interface and (ii) to provide an analysis of the effect of cholesteric ordering on the interfacial tension of the Ch/I interface. It is possible that other mechanisms based on polydispersity also contribute to the interfacial tension. Fluctuations are not taken into account in this note. It should be noted that fluctuations at the nematic/solid or gas interface have been proposed as the mechanism to explain the complex temperature dependence of γ.[13]

Uniaxial cholesteric liquid crystals are chiral nematics[10] whose equilibrium structure in a rectangular coordinate system (x,y,z) is given by the following director field $\mathbf{n}_0$:

$$\mathbf{n}(z) = (\cos q_0 z,\ \sin q_0 z,\ 0); \quad q_0 = \frac{2\pi}{P_0} \qquad \text{(1a,b)}$$

where q_0 is the equilibrium wave vector, and P_0 is the equilibrium pitch or distance over which the director rotates by 2π radians. The sign of q_0 indicates whether the cholesteric helix is right- or left-handed. The pitch is in the micron range, and as mentioned above, it is affected by concentration, pressure, and temperature.[10] In this note we shall adopt the simplifying assumption that the cholesteric is always uniaxial, although biaxiality is known to affect the magnitude of the interfacial tension.[5] The presence of an interface such as the Ch/I will introduce gradients in the degree of molecular ordering as well as in the macroscopic director orientation. Under uniaxiality the cholesteric structure is captured by the symmetric traceless tensor order parameter $\mathbf{Q}$:

$$\mathbf{Q} = S(\mathbf{nn} - \delta/3) \qquad (2)$$

To describe the cholesteric−isotropic phase transition, we shall use the following uniaxial version of the Landau−de Gennes free energy density:[12]

$$f = f_\mathrm{h} + f_\mathrm{g} \qquad \text{(3a)}$$

$$f_\mathrm{h} = \frac{a}{2}\Big[(\nu^* - \nu) - \frac{2}{a}L_1 {q_0}^2\Big]S^2 - \frac{B}{3}S^3 + \frac{C}{4}S^4 \qquad \text{(3b)}$$

$$f_\mathrm{g} = S^2\Big[L_1 + \frac{1}{2}L_2\Big](\nabla\cdot\mathbf{n})^2 + S^2 L_1(\mathbf{n}\cdot\nabla\times\mathbf{n} - q_0)^2 + S^2\Big[L_1 + \frac{1}{2}L_2\Big]|\mathbf{n}\times\nabla\times\mathbf{n}|^2 + \frac{1}{3}\Big[L_1 + \frac{1}{6}L_2\Big](\nabla S)^2 + \frac{L_2}{6}(\mathbf{n}\cdot\nabla S)^2 + SL_2\Big[(\nabla\cdot\mathbf{n})(\mathbf{n}\cdot\nabla S) + \frac{1}{2}(\mathbf{n}\times\nabla\times\mathbf{n})\cdot\nabla S\Big] \qquad \text{(3c)}$$

where a, B, C, L_1, and L_2 are constants, ν is the polymer concentration, and ν^* is the limit of metastability of the isotropic phase. The cholesteric−isotropic transition concentration ν_{ci} and order parameter S_{ci}, obtained by

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* Corresponding author. e-mail c3co@musica.mcgill.ca; tel (514) 398-4196; Fax (514) 398-6678.

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minimizing f_h with $f_g = 0$, is given by

$$\nu_{ci} = \nu^* - \frac{2B^2}{9aC} - \frac{L_1 q_0^{\ 2}}{a} \tag{4a}$$

$$S_{ci} = \frac{2B}{3C} \tag{4b}$$

which indicates that helical ordering in lyotropic liquid crystals decreases the critical concentration. The first important results of this brief report are (a) that in lyotropic liquid crystalline systems cholestericity increases ordering, (b) it decreases the Ch/I transition concentration ν_{ci}, and (c) the scaling is given by $\nu_{ci} = \nu_{ci}(1/P_0^2)$. These results indicate that the Ch/I transition differs from the N/I transition due to the presence of helical ordering.

We next consider the interfacial tension γ_{ci} of the cholesteric–isotropic planar interface at ν_{ci} when the pitch P is equal to the equilibrium pitch P_0 and independent of the scalar order parameter S. Let the unit normal to the interface $\mathbf{k}$ be along z. For biphasic cholesteric–isotropic equilibrium at ν_{ci}, the homogeneous and gradient free energy densities become[6,12]

$$f_h = \frac{C}{4} S^2 (S_{ci} - S)^2 \tag{5a}$$

$$f_g = \left\{ \left(\frac{6L_1 + L_2}{4} \right) + \frac{3L_2}{4} (\mathbf{n}\cdot\mathbf{k})^2 \right\} \left(\frac{dS}{dz} \right)^2 \tag{5b}$$

The interfacial tension is given by[12]

$$\gamma_{ci} = \int_{-\infty}^{+\infty} (f_h + f_g)\, dz \tag{6}$$

The elastic constant L_2 can be expressed in terms of the well-known Frank elastic constants[10] of splay/bend (K) and twist (K_{22}) as follows:

$$L_2 = \frac{K - K_{22}}{S^2} \tag{7}$$

For rodlike liquid crystals it is known that the twist constant (K_{22}) is smallest[10] and therefore $L_2 > 0$. Thus, this model predicts that the helix is oriented along the unit normal, and the director is parallel to the interface: $\mathbf{n}\cdot\mathbf{k} = 0$. This result is in agreement with predictions of molecular theories[2,5,9] and with experiments.[9] Performing the integration, the well-known result[12] is found:

$$\gamma_{ci} = \frac{1}{12} \left(\frac{6L_1 + L_2}{2} \right)^{1/2} S_{ci}^{\ 3} \sqrt{C} \tag{8}$$

The order parameter across the interface is given by

$$S(z) = \frac{S_{ci}}{1 + \exp(-z/\xi)}; \quad \xi = \sqrt{\frac{6L_1 + L_2}{2S_{ci}^{\ 2} C}} \tag{9a,b}$$

where ξ is the correlation length, and gives the magnitude of the interfacial region thickness. The order of magnitude of ξ is on the nanometer scale and is much smaller than the equilibrium pitch P_0 of the cholesteric helix, which is on the micrometer scale. Thus, we can conclude that order parameter effects do not couple with pitch variations because of the disparate length scales. Using typical parameter values,[10,15] we found that γ_{ci} is of the order of 10^{-2} mN/m. This result can be found in the review of Yokoyama.[6] The order of magnitude predicted by the Landau–de Gennes theory is in agreement with molecular theories,[2–5,9] but undepredicts experimental results,[9] by an order of magnitude. Thus, we reach the conclusion that an effect not contained in nematic ordering must be responsible for the observed discrepancy.

A key experimental finding that points toward the resolution of the mentioned discrepancy is the deviation of the pitch from its equilibrium value: $P \neq P_e$. A key observation of the experimental results (Figure 3 in the paper of ref 9) is that close to the Ch/I interface the pitch is smaller than far from the interface. Thus, experiments show that indeed $P = P(z)$. This experimental observation[9] agrees with recent measurements[14] of the pitch in two-component mixtures and pure low molar mass cholesteric liquid crystals. In that work[14] it was established experimentally that

$$\frac{1}{P} = \frac{1}{P_I}(1 + \alpha S); \quad q = q_I(1 + \alpha S) \tag{10a,b}$$

where P_I is the pitch in the isotropic phase, α is a negative constant, and S is the scalar order parameter. Thus, the measurements reported in ref 14 imply that if S is spatially nonhomogeneous, so is the pitch, in full agreement with the experiments reported in ref 9. In addition, it was established[14] that the parameter α is negative, so that the pitch in the isotropic phase is smaller than the pitch in the cholesteric phase:

$$P(S>0) > P_I = P(S=0) \tag{11}$$

again in full agreement with the experiments of ref 9. Next we use eq 10b to characterize the contribution of the spatially varying pitch to the cholesteric free energy. To be consistent with experiments,[9,14] the homogeneous free energy now reads

$$f_h = \frac{a}{2}\left[(\nu^* - \nu) - \frac{2}{a} L_1 q^2 \right] S^2 - \frac{B}{3} S^3 + \frac{C}{4} S^4 \tag{12}$$

where q is now given by eq 10b. Thus, the fact that $q = q(S)$ and at the Ch/I phase transition there is necessarily a gradient in S, the coefficients of the bulk free energy density are renormalized by a pitch dependent function, as follows:

$$f_h = \frac{a}{2}\left[(\nu^* - \nu) - \frac{2}{a} L_1 q_I^{\ 2} \right] S^2 - \frac{B_c}{3} S^3 + \frac{C_c}{4} S^4 \tag{13a}$$

$$B_c = B + 6L_1 q_I^{\ 2} \alpha; \quad C_c = C - 4L_1 q_I^{\ 2} \alpha^2 \tag{13b}$$

Since α is negative, we find

$$B_c < B; \quad C_c < C \tag{14}$$

and for sufficiently large α the decrease in C will be greater than in B, since $B \approx C$.[15] Assuming no new contributions from long-range elasticty, following exactly the same procedure as above we find that the interfacial tension now reads

$$\gamma_{ci} = \frac{1}{12} \left(\frac{6L_i + L_2}{2} \right)^{1/2} \hat{S}_{ci}^{\ 3} \sqrt{C_c}; \quad \hat{S}_{ci} = \frac{2}{3} \frac{B_c}{C_c} \tag{15a,b}$$

To quantify the effect of cholesteric ordering on the interfacial tension in reference to the nematic ordering, we compute the ratio γ_{ci}/γ_{Ni} and find

$$\frac{\gamma_{ci}}{\gamma_{Ni}} = \left\{\frac{1 + \frac{6L_1}{B}(q_I^{\,2}\alpha)}{1 - \frac{4L_1}{C}(q_I^{\,2}\alpha^2)}\right\}^3 \sqrt{1 - \frac{4L_1}{C}(q_I^{\,2}\alpha^2)} \qquad (16)$$

Using typical values $B = 2C/3 = 10^4$ J/m^3,[15] $L_1 = 10^{-11}N - 10^{-12}N$,[15] $q^2 = 10^{14}$ m^{-2},[14] and $\alpha = -3$,[14] it is found that $\gamma_{ci}/\gamma_{Ni} = 5$. In other words, the increase is due to an increase of the order parameter at the interface: $\hat{S}_{ci} > S_{ci}$. Thus, the interfacial tension of the cholesteric/isotropic interface is greater than the nematic–isotropic interface approximately by a factor of 5–10. This result is consistent with ref 9. Modifications of eqs 4 and 9 due to pitch variations $q(S(z))$ are straighforward:

$$\nu_{ci} = \nu^* - \frac{2B_c^2}{9aC_c} - \frac{L_1 q_I^{\,2}}{a} \qquad (17)$$

$$S(z) = \frac{\hat{S}_{ci}}{1 + \exp(-z/\hat{\xi})}; \quad \hat{\xi} = \sqrt{\frac{6L_1 + L_2}{2\hat{S}_{ci}^2 C_c}} \qquad (18a,b)$$

In summary, in this brief note we have shown (i) that the Landau–de Gennes theory predicts that the pitch of a cholesteric decreases the critical concentration at which the cholesteric-isotropic transition sets in, by a quantity proportional to the pitch squared, (ii) that for rodlike cholesterics the cholesteric helix orients normal to the cholesteric–nematic interface, and (iii) in the absence of pitch gradients the interfacial tension of the Ch/I interface is of the order of 10^{-2} mN/m. In addition, (iv) we have shown that the experimentally observed pitch gradients close to the interface can be attributed gradients of the scalar order paramater, and (v) the contributions of pitch gradients to the interfacial tension appear through a renormalization of the homogeneous free energy density coefficients and tend to increase it by an amount that is consistent with the experimental data. Finally, other effects not considered in this brief note, such as polydispersity, fluctuations, and concentration gradients, may also contribute to the magnitude of the interfacial tension and are worthy of further investigation.

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