Entropically driven reentrant SmC-SmA-SmC phase transition in composite polymer–liquid crystal systems

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I consider the effects of polymers on the smectic phase of a host liquid crystal matrix. Focusing on the regime in which the polymers are predominately confined between the smectic layers, I find that the presence of the polymers can lead to a reentrant phase diagram with the smectic-C sandwiching the smectic-A phase from both the high and low temperature sides. Simple entropy-energy arguments predict the shape of the reentrant phase boundary.

Recently, some of the attention in liquid crystal research has focused on composite polymer–liquid crystal systems, with the aim of expanding the range of applications of liquid crystals by controlling the electro-optical properties and phase behavior.

This theoretical interest in such systems is motivated by recent experiments in which a two-component smectic liquid crystal–monomer mixture is found to segregate into monomer–rich layers confined between the smectic-A (SmA) layers [1]. In these experiments a significant increase in polymerization rate was observed when polymerization was initiated within the smectic phase of the liquid crystal host. The confining smectic layers are thought to lead to a two-dimensional (2d) organization of monomers between the layers, thereby enhancing the polymerization rate. It is believed that the final polymerized state is dominated by configurations in which polymers are confined between the smectic layers. Similar segregation of organic solvents intercalated between the smectic layers of a host thermotropic smectic liquid crystal was observed in recent X-ray experiments by Rieker [2].

In this paper I examine how the presence of the polymers confined between the smectic layers modifies the SmA and SmC regions of the phase diagram. I find that polymer presence can lead to the entropically induced reentrant SmC-SmA-SmC phase diagram displayed in Fig. 1.

The standard expression for the free energy of the smectic phase which allows for the possibility of developing the SmC order parameter \( \vec{C} \), describing a 2d projection of the nematogens onto the smectic layers is

\[
F_{\text{lc}} = \int \left[ \frac{K_1}{2} (\nabla_{\perp} u)^2 + \frac{B}{2} (\partial_z u)^2 + \alpha (\vec{\nabla}_{\perp} \cdot \vec{C})(\nabla_{\perp} u) \right. \\
+ \left. \frac{J}{2} |\nabla \vec{C}|^2 + \frac{1}{2} (T - T_{AC}) |\vec{C}|^2 + \frac{u}{4} |\vec{C}|^4 \right]. 
\]

(1)

FIG. 1. The proposed phase diagram for the smectic liquid crystal with polymers confined between the smectic layers as a function of temperature \( T \) and the polymer density \( n \).

The first two terms describe the smectic elasticity. The third term describes the energetic tendency of the local inhomogeneity in the tilt order parameter to induce the local layer extrinsic curvature, which screens the nonuniformity in \( \vec{C} \). The last three terms are the contribution due the SmC tilt order, which develops for \( T < T_{AC} \) via a well studied continuous phase transition in the 3d XY universality class that has been extensively studied and is quite well understood [3]. Within the SmC phase, the order parameter \( \vec{C} \) can be integrated out and the resulting elastic free energy is similar to the SmA free energy except for the in-plane anisotropy, generated by the average molecular tilt.

How is the well-studied Nematic-SmA-SmC phase diagram modified by the presence of polymers? Obviously the smectic will swell in the \( z \)-direction, leading to a \( T \)-and polymer density \( n \)-dependent liquid crystal density modulation wave vector \( q_0(T, n) = 2\pi/d(T, n) \). The layer spacing \( d(T, n) \) will increase with \( T \) and \( n \), variation of which should be observable in X-ray scattering experiments [4]. The dependence of \( d(T, n) \) on \( n \) can be simply evaluated [4] by assuming for simplicity that large fraction of added polymer is concentrated...
smectic layers (an assumption consistent with the experimental observations) [1]. Assuming pure SmA order I estimate $d = d_0 + \Delta d_0 = d_0 (1 + f_v)$, where $f_v = V_p/V_c$ is the polymer-to-liquid crystal volume fraction. The $T$-dependence can be obtained from the estimate of the entropic polymer pressure (see below).

A much more interesting consequence (that is likely to dominate in a confined geometry of e.g. a liquid crystal display) is that polymers, confined by the smectic layers, will force the nematogens to tilt relative to the smectic layer normal. This tilt will increase the effective space available for polymer diffusion between the confining layers, thereby lowering the entropic polymer pressure (see Fig. 2). Therefore such entropic polymer-smectic interaction will induce a local SmC order parameter $\bar{C}$, which can develop into a true long-range order.

The reentrant behavior can therefore be understood in the following way. For $T >> T_{AC}$, the increase in the total free energy due the confinement of polymers is large and can be accommodated by developing SmC order, thereby stabilizing SmC phase over the SmA phase. In the intermediate $T$ range, however, the polymers’ tendency for diffusion and therefore the entropic interaction is suppressed and the SmA phase is again stabilized. Finally, for $T < T_{AC}$ the SmC is stabilized over the SmA phase, as in the polymer-free liquid crystal.

To support above physical arguments I calculate the entropically-induced polymer interaction $\delta F_p$ for the SmC order parameter. I take the center of mass layer spacing to be $d = d_0 + \Delta d$, with $\Delta d$ to be determined below, and consider the decrease in polymer entropy due to the confinement of spacing $Z_o$ in the $z$-direction (related to $|\bar{C}|$).

In the absence of confinement a polymer of length $L$ would explore a 3d region of space whose extent in the $z$-direction is in general $R_G \sim l_p(T)(L/l_p(T))^{\nu_z}$, where the wandering exponent $\nu_z$ and the persistent length $l_p(T)$ are determined by polymer interaction, and by the relevant range of $L$ related to the smectic spacing $d$ and polymer elasticity (see below). For the smectic confinement of width $Z_o$, a polymer will typically make collisions with the smectic layers every $L_o \sim l_p(T)^{1/\nu_z} z_o^{1/\nu_z}$ of internal length. In the total length $L$ of a single polymer these excursions will on average result in $N_c \sim L/L_o \sim L l_p(T)^{1/\nu_z} Z_o^{1/\nu_z}$ collisions with the smectic layers. Since upon each of these (predominantly) reflecting collision the polymer is prevented from continuing along the $z$-direction, each encounter with the smectic layer leads to entropy reduction by $s \approx \log 2$. The corresponding total increase in the free energy density is given by

$$\delta F_p \sim T n s N_c \sim \left( T l_p(T)^{1/\nu_z - 1} / Z_o^{1/\nu_z} \right) n s d ,$$

where $n$ is the 3d density of polymers.

As can be seen from Fig. 2 the SmC order parameter is directly related to the maximum allowed excursion $Z_o(|\bar{C}|) = d - \sqrt{a^2 - |\bar{C}|^2}$, where $a$ is the length of the liquid crystal molecule. Combining this expression with Eq. 2, assuming for simplicity that $|\bar{C}|^2 \ll a < d_0$ and $\Delta d_0 \ll d_0$, and expanding in these small quantities, I find

$$\delta F_p \approx \text{const} - \frac{1}{2} T l_p(T)^{1/\nu_z - 1} \tilde{n} (|\bar{C}|^2 + 2a \Delta d) ,$$

where $\tilde{n} = (2nsL) / (\nu_z a (d_0 - a)^{(1/\nu_z + 1)})$ and obviously from Fig. 2 $d_0 > a$.

As argued in the introduction and expected on physical grounds, this entropically induced part of the free energy can be reduced by swelling the layers $(d) \Delta d > 0$ and/or by inducing the SmC order $|\bar{C}| > 0$. The value of the swelling $\Delta d$ can be roughly determined by balancing the above negative free energy against the positive elastic strain energy $E_e \sim (B/2)/(\delta d/d_0)^2$, ($B$ is the compressional bulk modulus), giving

$$\Delta d(T) \approx T l_p(T)^{1/\nu_z - 1} \tilde{n} a d_0^2 / B ,$$

This increase in the layer spacing $d$ leads to a ($\bar{C}$-independent) reduction of the above free energy by an amount $(T l_p(T)^{1/\nu_z - 1} \tilde{n} a d_0^2)/(2B)$.

To learn how the presence of polymers affects the liquid crystal smectic part of the phase diagram I combine the entropically induced free energy in Eq. 2 with the liquid crystal smectic free energy $F_{lc}$ from Eq. 1 and focus on the tilt order parameter $\bar{C}$ part of the resulting free energy $F_C$.

$$F_C = \frac{1}{2} \int \left[ J |\nabla \bar{C}|^2 + (T - T_{AC} - \tilde{n} T l_p(T)^{1/\nu_z - 1}) |\bar{C}|^2 + \frac{u}{2} |\bar{C}|^4 \right] .$$

By minimizing the free energy $F_C$ it is easy to see that the SmA phase, characterized by $\langle \bar{C} \rangle = 0$, is stable.
in that part of the phase diagram where the coefficient $(T - T_{AC} - nT_\nu(T)^{1/\nu-1})$ of the quadratic term in $F_C$ is positive. The transition to the SmC phase, where $\langle \hat{C} \rangle \neq 0$ takes place when this coefficient changes sign and becomes negative.

For a vanishing polymer density $\tilde{n} = 0$ the quadratic coefficient is simply $T - T_{AC}$ and the SmA-SmC transition occurs at a unique temperature $T_{AC}$, with the SmA stable at $T > T_{AC}$ and SmC order developing for $T < T_{AC}$. However, in the presence of polymers ($\tilde{n} \neq 0$), depending on the $T$ dependence of $l_p(T)$ and the polymer density $\tilde{n}$, it is possible for this quadratic coefficient to vanish at a more than one root, corresponding to a reentrant phase diagram for the SmA and SmC phases, of the type displayed in Fig.1. Assuming that generically $l_p(T) \sim e^{T/\nu}$, it is easy to see that for $\alpha \equiv (1/\nu - 1) > 0$ there will be two roots, for $\tilde{n} < \tilde{n}^*$. For example for $\alpha = 1$ these roots can be easily found analytically $T_{AC}^+(\tilde{n}) = (1 + (1 - 4\tilde{n}T_{AC})^{1/2})/(2\tilde{n})$, and for the high- and low-$T$ parts of the phase boundary of the reentrant transition, respectively. For a general $\alpha$ the complete phase diagram in the $n - T$ plane is defined by the phase boundary,

$$\tilde{n}(T) = (T - T_{AC})/e^{T/\nu T_{AC}}$$

which for $\alpha > 0$ exhibits a reentrant behavior illustrated in Fig.1 with the SmA phase sandwiched by the SmC phase on both the low- and high-$T$ sides. For $\alpha \leq 0$ the transition is not reentrant but $T_{AC}(n)$ increases with the increased polymer concentration. This latter scenario is an entropic analog of the compression induced SmA-SmC transition discovered experimentally over 20 years ago by Riboto et al. [1].

As expected for $\alpha > 0$ the lower transition $T^-(n)$ approaches $T_{AC}$ of a pure liquid crystal as $n \to 0$, and near $T_{AC}$ the phase boundary is a linearly-increasing function of $n$. The transition temperature $T_{CA}^+ \to \infty$, for a vanishing polymer density, however this behavior gets interrupted at $\tilde{n} = \tilde{n}_c \equiv (T_{NA} - T_{AC})/\epsilon T_{NA}^2$ and $T_{CA}^+(\tilde{n}_c) \approx T_{NA}$, where the N–SmA phase boundary gets encountered (see Fig.2). For $\tilde{n} < \tilde{n}_c$ the transition goes directly from the nematic to SmA, followed by the standard SmA–SmC transition. From Eq.3 and Fig.1, it is clear that the reentrant transition, together with the SmA phase disappears for $\tilde{n} > \tilde{n}_c \equiv \gamma^*/(\alpha + 1)T_{AC}^\alpha$.

It is useful at this stage to examine a simple model of a polymer in order to extract the $T$ dependence of $l_p(T)$ and the resulting prediction for the shape of the phase boundary. At short scales a polymer exhibits an energetic rigidity against bending with a bending modulus $\kappa$, and can be described by an effective free energy $F_1 \approx \frac{1}{2} \int ds(\partial \theta/\partial s)^2 \approx \frac{1}{2} \int ds(\partial^2 \vec{r}/\partial s^2)^2$. In a length $L$ smaller than an orientational persistent length $l_{p1}(T)$, the polymer will explore an angular range $\theta_{rms} \approx LT/\kappa$, corresponding to transverse deviations $R_G \approx \theta_{rms} L \sim \sqrt{T/k}L^{3/2}$. This implies that $l_{p1}(T)$, length up to which above model is valid and the polymer behaves as a directed one, is $l_{p1}(T) = \min(\kappa/T, a_0)$, where $a_0$ is the minimum length set by the inter-monomer distance. For this range of length scales ($< l_{p1}(T)$), assuming $\kappa/T > a_0$, I therefore find $\beta = -1$, $\nu_z = 3/2$, $\alpha = 1/3 > 0$, implying a reentrant SmC–SmA–SmC transition.

In thermotropic smectics the interlayer spacing $d$ is a microscopic length scale on the order of few angstroms and therefore a typical length $L_0$ of a section of a confined polymer between the collisions with smectic layers will be smaller than $l_{p1}(T)$, implying the reentrant behavior illustrated in Fig.1. For the lyotropic smectics, however, where the interlayer spacing can be significantly larger, the polymer collision length $L_0$ will typically be larger than $l_{p1}(T)$. For this $L_0 >> l_{p1}$ regime a more appropriate model is that of a coiled polymer with an entropically generated elastic modulus $\sigma(T) \approx T/l_{p1}(T)$. In this regime the effective free energy describing polymer conformation is $F \approx \frac{2}{\epsilon} \int ds(\partial \vec{r}/\partial s)^2$ and leads to $R_G \sim \sqrt{T/\sigma(T)}L^{1/2} \sim \sqrt{l_{p1}(T)T^{1/2}}$. Assuming $l_{p1} = \tilde{n}_c > a_0$, for this regime I find $\beta = -1$, $\nu_z = 1/2$, $\alpha = 1 > 0$. At high $T$ and for low-rigidity polymers with small $T$-independent persistent length $l_{p1} = a_0$ $\beta = 0$, $\nu_z = 1/2$, and $\alpha = 0$. Both cases imply a single non-reentrant SmA–SmC transition, with $T_{AC}(n)$ monotonically shifting to higher $T$ with increasing polymer concentration.

When additional thermal fluctuations of the $\hat{C}$ order parameter are taken into account, as usual, the mean-field exponents and the actual shape of the phase boundary will be quantitatively modified. Based on general symmetry arguments, I expect that both the high- and low-$T$ transitions will be in the same universality class, that of the 3d XY model, which describes the conventional (polymer-free) SmA-SmC transition [3]. It is unfortunately difficult to make precise, model independent quantitative predictions of how these additional fluctuations will modify the reentrant phase boundary, except to argue that they will tend to partly wash it out. Nevertheless it is likely that even in the presence of these additional fluctuations, the reentrant behavior and the upward $T_{AC}(n)$ shift with increasing $n$, discussed here, should still be observable in thermotropic and lyotropic liquid crystals, respectively.

A more important obstacle to observing the reentrant phase diagram proposed here lies in the Eq.5 Maximizing $\langle n \rangle$ with respect to $T$, one can easily show that the turning point of this phase boundary (responsible for reentrant behavior) occurs at $T^* = T_{AC}(\alpha + 1)/\alpha$, which is unfortunately too high of a temperature to be experimentally observable in common liquid crystal systems with $T_{AC} \approx 300K$. At such high $T$, the entropic effects discussed here will be dominated by other ther-
mal effects such as for example the transition into the isotropic phase and 3d deconfinement of polymers. However, as discussed above, it is likely that the shape and therefore the $T_{\text{AC}}(\alpha + 1)/\alpha$ estimate for the maximum in the phase boundary will be modified by fluctuations, possibly allowing the reentrance to be observable in some liquid crystal systems.

Finally, one additional scenario is possible. As argued in this paper, the reentrance mechanism is driven by the fact that at high $T$ the tilt in the SmC phase is more favorable for accommodating the out-of-plane undulation of the confined polymers, thereby lowering their free energy. However, for this accommodation to take place it is not necessary to have long-range order in the SmC order parameter; all that is necessary is tilt, without $\vec{C}$ directional long-range correlations. Therefore it is possible that the high $T$ part of the SmC phase in Fig. 2 is replaced by the SmA phase with an enhanced local $C$ order, $<|\vec{C}|> \neq 0$, but with $<\vec{C}> = 0$ due to random $\vec{C}$ orientations. In this case the high temperature $T_{\text{CA}}$ transition will be replaced by a crossover or a first order transition within SmA phase.

In summary, I have argued that the smectic part of a liquid crystal phase diagram can be considerably modified by the presence of polymers, confined between the smectic layers. I have shown that this confinement generates an effective entropic interaction which can lead to a reentrant SmC–SmA–SmC phase diagram.

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