Imprinted Networks as Chiral Pumps

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We investigate the interaction between a chirally imprinted network and a solvent of chiral molecules. We find, a liquid crystalline polymer network is preferentially swollen by one component of a racemic solvent. This ability to separate is linked to the chiral order parameter of the network, and can be reversibly controlled via temperature or a mechanical deformation. It is maximal near the point at which the network loses its imprinted structure. One possible practical application of this effect would be a mechanical device for sorting mixed chiral molecules.

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Chirality is of vital importance in pharmacology and chemical biology. Sorting right handed from left handed molecules is a common and yet tricky process \[1,2\]. Traditionally, mixtures of chiral molecules are separated using other chiral molecules with intrinsic chirality \[2\] which is often difficult to control. Liquid crystalline elastomers with an imprinted chirality offers an alternative solution.

Recently we proposed a theory of chiral imprinting in liquid crystalline polymer networks \[3\] where nematic polymers are crosslinked in the presence of chiral solvent, that is when they have an induced cholesteric phase. Subsequent removal of the solvent, and thus all of the intrinsically chiral material, can either leave behind a cholesteric network or see the network lose its chiral structure, depending on the strength of a chiral order parameter, \(\alpha\) (see below). Above a critical point at \(\alpha_c = 2/\pi\), director twist is lost in a second order manner. Experiments have shown conclusively that imprinting can be achieved \[3\]. The mechanical behaviour of such imprinted solids and similar cholesteric nematic networks has been analysed \[2\]. Imposed strain induces the director to rotate and eventually eliminates twist. Thus, mechanical deformation can modify and even destroy the chiral structure. For an imprinted network, this can mean the complete loss of chirality (in contrast to intrinsic materials that would thereby simply enter an untwisted chiral nematic phase, \(N^*\)). Imprinted networks hence offer chirality that can be controlled externally. In this article, we calculate the interaction between the imprinted chiral elastomer and a racemic solvent which is used to swell the network or see the network lose its chiral structure, deforming the sample. This gives rise to the possibility of mechanical devices to sort a racemic solvent.

In a cholesteric, the local order is similar to that of a uniaxial nematic with director \(n\) (which then takes angles \(\theta_n = q_r x\) with respect to \(z\) in the \(yz\) plane as it advances in a helix). A model for the total free network energy per chain, \(F_n\), in a nematic elastomer is a simple generalisation \[4\] of classical Gaussian rubber elasticity:

\[
F_n = \frac{k_B T}{2} \text{Tr} \left[ I_n - \frac{1}{2} \frac{\partial^2}{\partial n} \right].
\]

The reduced molecular shape tensors \(I_n\) and \(l\) before and after deformation record the director and the intrinsic anisotropy, \(r\): \(l_n = (r - 1) n \otimes n + l\) and (the inverse) \(l^{-1} = (\frac{1}{r} - 1) n \otimes n + l\).

As a result of swelling, we expect the deformation tensor \(A\) to consist of a uniform expansion and a uniaxial, volume-preserving deformation along the pitch axis, \(z\):

\[
A = \Phi^{-1/3} \left( \lambda^{-1/2} I + \left( \lambda - \lambda^{-1/2} \right) z \otimes z \right),
\]

reflecting that, on coarse graining, the cholesteric is uniaxial about the pitch axis. \(\Phi\) is the volume fraction of network after swelling. The volume \(V_o\) of the network increases to \(V_o/\Phi\) with the additional solvent.

Substituting (2) and (3) into (1) leads to:

\[
2\Phi^{2/3} \frac{F_n}{k_B T} = \frac{1}{\lambda} \frac{(r - 1)^2}{r} \sin^2(\theta - q_r x) + \lambda^2 + \frac{2}{\lambda}.
\]

The \(\sin^2\) term gives the director anchoring to the network. For small rotations, \(\omega\), relative to the matrix it gives the \(D_1 \omega^2\) term of the de Gennes continuum mechanics approach \[4\]. Note that without network anchoring, \(\partial F_n/\partial \lambda\) leads to \(\lambda = 1\) and there is no tendency to relax shape (at a given dilation). From the \(\sin^2\) term, we deduce that the anchoring coefficient after swelling, \(D_1\), is related to that before swelling \(D_1\):

\[
\frac{\Phi^{1/3}}{\lambda} D_1 = \frac{(r - 1)^2}{r} Y_o; \quad D_1 = \frac{(r - 1)^2}{r} Y_o.
\]

with the chain density defined as \(n_n = \frac{N}{r^2}\), the network shear elastic constant being \(Y_o = n_n k_B T\), and \(N\) being the total number of chains.

In the Frank energy, \(F_f\), we retain only twist:

\[
\frac{2\Phi}{V_o k_B T} F_f = (n \cdot \nabla \times n + q)^2 \equiv (-d\theta/dx + q)^2.
\]
For simplicity we assume the local nematic order, and therefore $K_2$, remain unchanged during swelling - for instance if the chiral solvent has the same nematogenic properties as the polymer’s own nematogenic elements. The pitch wave vector $q$ will be different from the originally imprinted $q_o$, due to deformation $\Phi^{1/3}/\lambda$ along the $x$ axis from swelling and shape change. The solvent chirality, $q_s$, further modifies $q$:

$$ q = \frac{\Phi^{1/3}}{\lambda} q_o - q_s (2\phi - 1) . $$

Thus the first term corresponds to geometry and the second to the left-right imbalance of the solvent; the volume fractions of the left and right handed solvents are $\phi_l = \phi$ and $\phi_r = 1 - \phi$. The difference from racemic, $\phi = 1/2$, allows the twist, $\pm q_s$, of the enantiomers to express itself.

Imprinting is then a competition between the elastic anchoring energy, $F_n$, which resists director rotation away from the direction in which it was formed, and the Frank energy, $F_f$, which drives $d\theta/dx$ towards the current chiral twist $q$. If $q$ is different from the value $q_o$ remembered by the network, then twist towards this new value may occur depending upon whether the anchoring, $D_1 q^2$ or the Frank, $K_2$ energy prevails. This balance is quantified by $\tilde{\alpha}$, the geometric ratio of the two energy scales:

$$ \tilde{\alpha} = \sqrt{\frac{K_2}{D_1}} q = \frac{\sqrt{\alpha}}{q_o} ; \quad \alpha_o = \sqrt{\frac{K_2}{D_1}} q_o . $$

In reference [3], chiral solvent was replaced altogether, leaving a Frank penalty $K_2 q_o^2$. Imprinting was successful for $\alpha_o < 2/\pi$ and the twists were retained. Above $2/\pi$ one must optimise over $\theta$-profiles to find the minimal free energy, and some untwisting occurs (the efficiency of imprinting is < 1, see figure [3]).

Next we compare $\tilde{\alpha}$ with $2/\pi$ and examine the preferential absorption of one handedness over the other.

![Imprinting efficiency vs. network parameter $\alpha$. The slope at the critical point $\alpha = \alpha_o$ diverges.](image)

The mixing free energy density can be written as:

$$ f_m = n_m k_BT [\chi_{tr} \phi(1 - \phi)(1 - \Phi)^2 + \phi(1 - \Phi) \ln \phi + (1 - \phi)(1 - \Phi) \ln (1 - \phi) + (1 - \Phi) \ln (1 - \Phi) + \chi_{rn} (1 - \Phi)(1 - \Phi) + \chi_{rn} (1 - \Phi)(1 - \Phi)] $$

where $n_m = 1/v_m$ is the solvent number density (with $v_m$ the volume occupied by a single solvent molecule). The usual $\chi$ interaction parameters describe the interaction of left and right molecules with each other ($lr$) and with the network ($ln$ and $rn$). The latter are equal by symmetry if the network polymers are achiral. The free energy of the entire system is:

$$ F = N F_n + F_f + \frac{V_o}{\Phi} f_m . $$

As in the case of imprinting, we need to minimise energy over the profile of nematic director orientation $\theta$ as we go down the pitch axis. We can do this first since the mixing part does not contain $\theta$, and then we need to find the optimal $\lambda$. We do this separately for different regimes of imprinting parameter $\tilde{\alpha}$.

**The small $\tilde{\alpha}$ limit.** In this regime of high imprinting efficiency, the director distribution is preserved. Thus there is no $D_1$ penalty, but a Frank penalty for not having the currently desired twist $q$:

$$ f(\phi, \lambda) = F\Phi/V_o = \frac{K_2}{2} \phi^2 + \frac{\Phi^{1/3}Y_o}{2} (\lambda^2 + \frac{2}{\lambda}) + f_m $$

where $f_m = F_m/\Phi/V_o$, and $q$ depends on solvent composition, see eq. (6). Minimising $f$ over $\lambda$ gives a 4th order polynomial equation in $\lambda$ (given the $\lambda$ dependence of $q$):

$$ - K_2 q_o^2 + Y_o (\lambda - \frac{1}{\lambda}) = 0 . $$

However, assuming the uniaxial relaxation $\epsilon = \lambda - 1$ is small, one can easily solve the above:

$$ \epsilon \approx - \frac{K_2}{Y_o} (\phi^{1/3} q_o - q_s (2\phi - 1)) q_o . $$

Typically, $K_2 \sim 10^{-11}$N, $Y_o \sim 10^5$Pa and $q_{o,s} \sim 10^5$m$^{-1}$ and it appears that the assumption of small $\epsilon$ ($\sim 10^{-3}$) applies to most materials. Note that the explicit $\Phi$ dependence has vanished in this limit, and the shape relaxation is independent of the degree of swelling except indirectly through $\phi$. Substituting $\lambda \approx 1$ back, we have:

$$ f(\phi) = \frac{K_2}{2} \phi^2 + \frac{3\Phi^{1/3}}{2} Y_o + f_m $$

where $\Phi = \Phi^{1/3} q_o - q_s (2\phi - 1)$. The chemical potential difference $\Delta\mu = \mu_l - \mu_r = (1/[n_m(1 - \Phi)]) \partial f/\partial \Phi$ is:

$$ \frac{\Delta\mu}{k_BT} = \eta + \chi_{tr}(1 - 2\phi)(1 - \Phi) + \ln \frac{\phi}{1 - \phi} $$

where $\eta = -2K_2 q_o/[n_m k_BT(1 - \Phi)]$. In the reservoir (no network, $\Phi \rightarrow 0$, $\phi_l \rightarrow \phi_o$ and $\phi_r \rightarrow 1 - \phi_o$), the mixing energy density $f_r$ is:

$$ \frac{f_r}{n_m k_BT} = \chi_{tr} \phi_o(1 - \phi_o) + \phi_o \ln \phi_o + (1 - \phi_o) \ln (1 - \phi_o) $$
which yields the chemical potential difference:
\[ \frac{\Delta \mu_r}{k_B T} = \frac{1}{n_m k_B T} \frac{\partial f_r}{\partial \phi_o} = \chi_{lr}(1 - 2\phi_o) + \ln \frac{\phi_o}{1 - \phi_o}. \]

We now equate this difference to that of the network:
\[ \chi_{lr}(1 - 2\phi_o) + \ln \frac{\phi_o}{1 - \phi_o} = \eta + \chi_{lr}(1 - 2\phi)(1 - \Phi) + \ln \frac{\phi}{1 - \phi}. \]

Suppose the \(\chi_{lr}\) terms are negligible and that \(K_2 \partial \eta \ll n_m k_B T\), \(i.e.\) \(\eta\) is small compared to 1. We then have for the l-concentration, \(\phi\), in the network, given \(\phi_o\) in the reservoir:
\[ \phi \approx \frac{1 - \eta}{1 - \eta \phi_o} \phi_o. \]

We should also equate the osmotic pressures \((\partial F/\partial \Phi)\) to determine the equilibrium values of \(\Phi\), in addition to the \(\phi\) obtained above. In practice, \(\Phi\) is readily fixed experimentally; we take it as a known system parameter.

The large \(\tilde{\alpha}\) limit. In this regime \((\tilde{\alpha} \gg 2/\pi)\) of low imprinting efficiency, the director unwinds to the currently desired twist \(q\). There is then no Frank penalty but a \(D_1\) penalty since the anchoring has been violated:\
\[ f(\phi, \lambda) = F\Phi/V_o = \frac{\tilde{D}_1}{4} + \frac{\Phi^{1/3}}{2} Y_o \left( \lambda^2 + \frac{2}{\lambda} \right) + f_m. \]

Minimisation over \(\lambda\) yields \(\lambda = [(r + 1)^2/4r]^{1/3}\) and the free energy:
\[ f(\phi) = \frac{3\Phi^{1/3} Y_o}{2} \left[ \frac{(r + 1)^2}{4r} \right]^{2/3} + f_m, \]
from which it follows that:
\[ \frac{\Delta \mu_r}{k_B T} = \chi_{lr}(1 - 2\phi)(1 - \Phi) + \ln \frac{\phi}{1 - \phi}. \]

Equating the chemical potential difference to \(\Delta \mu_r\) leads to the equilibrium value of \(\phi\). If we assume that the \(\chi_{lr}\) term is small so that \(\chi_{lr}^2\) and higher order terms in \(\chi_{lr}\) can be ignored, then the network \(\phi\), is close to that, \(\phi_o\), in the reservoir:
\[ \phi/\phi_o \approx 1 + \chi_{lr}(1 - 2\phi_o)(1 - \phi_o)\Phi. \]

The intermediate \(\tilde{\alpha}\) regime. In general, minimisation over the \(\theta\)-profile \(\tilde{\alpha}\) gives:
\[ f(\phi, \lambda) = g(\tilde{\alpha}) \tilde{D}_1/2 + \frac{\Phi^{1/3}}{2} Y_o \left( \lambda^2 + \frac{2}{\lambda} \right) + f_m \]
with the profile free energy \(g(\tilde{\alpha})\) given by:
\[ g(\tilde{\alpha}) = \tilde{\alpha}^2 \quad \text{for} \quad \tilde{\alpha} < 2/\pi \]
\[ = \tilde{\alpha}^2 - k^{-2} + 1 \quad \text{for} \quad \tilde{\alpha} > 2/\pi \]

and where \(k\) is related to \(\tilde{\alpha}\) via \(\tilde{\alpha} = 2E(k)/\pi k\), (see Fig. 3 for \(g\) and its derivative). \(E\) is the complete elliptic integral of the second kind. Minimisation of \(f(\phi, \lambda)\) over \(\lambda\) gives a condition for the optimum \(\lambda = \tilde{\lambda}\):
\[ \left[ \frac{\partial g}{\partial \tilde{\alpha}} \frac{\partial \tilde{\alpha}}{\partial \lambda} - \frac{g}{\lambda} \right] \frac{(r - 1)^2}{2 \lambda r} + \left( \lambda - \frac{1}{\lambda^2} \right) = 0 \]

EQUATING the network and reservoir exchange chemical potentials yields:
\[ - \gamma \frac{\partial g}{\partial \tilde{\alpha}} + \frac{1}{n_m k_B T} \frac{1}{1 - \Phi} \frac{\partial f_m}{\partial \phi} = \frac{1}{n_m k_B T} \frac{\partial f_r}{\partial \phi_o}, \]
where the prefactor \(\gamma\) is given by:
\[ \gamma = \frac{(r - 1)^2}{r} \frac{n_m}{n} \Phi^{1/6} \frac{q_s}{q_o} \frac{\alpha_o}{\lambda^{1/2}}. \]

Substituting the expressions for \(f_m\) and \(f_r\) leads to:
\[ - \gamma \frac{\partial g}{\partial \tilde{\alpha}} + \chi_{lr}(1 - 2\phi)(1 - \Phi) + \ln \frac{\phi}{1 - \phi} = \chi_{lr}(1 - 2\phi_o) + \ln \frac{\phi_o}{1 - \phi_o} \]

The first term on the left hand side of the equation is the contribution from the solvent-network interaction, which discriminates between the solvent handednesses. If \(\gamma\) and \(\Phi\) tend to zero, we recover the situation where \(\phi = \phi_o\).

![FIG. 2. Director profile free energy \(g(\tilde{\alpha})\) and derivative \(dg(\tilde{\alpha})/d\tilde{\alpha}\) (dashed line) against imprinting power \(\tilde{\alpha}\).](image-url)
Fig. 3 shows that $\phi > \phi_o$ is generally satisfied: the solvent handedness which agrees with the network is favoured for absorption. One can utilize this to devise a “pumping” cycle for extracting one component from a racemic mixture. An elastomer, exposed to a given mixture, preferentially absorbs one of the components. The solvent mixture, recovered from stretching the swollen elastomer and thereby switching off its chiral effect, can then be used in the next cycle of purification.

If we choose to fix the reservoir concentration $\phi_o = 0.5$ and vary the network’s imprinting power at formation, $\alpha_o$, we can see from figure 4 that the maximal resolving power is obtained when the imprinting power of the resulting network is near the transition point $\alpha = 2/\pi$.

Finally, we examine the effect of $\chi_{lr}$. It has been hitherto set to zero, that is we assume that any spontaneous tendency for the molecules of opposite handedness to demix is small. We see in figure 5 that a positive value of $\chi_{lr}$ favours demixing at small $\phi_o$. Repeated cycles of our chiral pump will push $\phi$ to the intersection of the curve with the line $\phi = \phi_o$.

We have shown that the chiral structures offered by imprinting allows one to preferentially absorb one handedness from a racemic mixture into a network. Moreover, since the chirality is mechanically tuneable and there is no material of intrinsic chirality in the network, one can then release by mechanical fields the absorbed solvent in which a chiral imbalance has been achieved.

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