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 that 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.

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 offer an alternative solution.

Recently we proposed a theory of chiral imprinting in liquid-crystalline polymer networks [3] where nematic polymers are cross-linked in the presence of chiral solvent, that is when they have an induced cholesteric phase. Subsequent removal of the solvent, and thus of all 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, α (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 [4]. The mechanical behavior of such imprinted solids and similarly cholesteric nematic networks has been analyzed [5]. 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 Letter, we calculate the interaction between the imprinted chiral elastomer and a racemic solvent which is used to swell the network. We show that the network has the ability to sort the components of a mixture according to their handedness, and this ability is a direct result of a chiral order parameter controllable by simply 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 $\underline{n}$ (which then takes angles $\theta_o = q_o x$ with respect to $\underline{z}$ 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 generalization [6] of classical Gaussian rubber elasticity:

$$F_n = \frac{k_B T}{2} Tr[\underline{\underline{l}}_o \underline{\underline{\lambda}}^T \underline{\underline{l}}^{-1} \underline{\underline{\lambda}}]. \quad (1)$$

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

As a result of swelling, we expect the deformation tensor $\underline{\underline{\lambda}}_d$ to consist of a uniform expansion and a uniaxial, volume-preserving deformation along the pitch axis, $\underline{x}$:

$$\underline{\underline{\lambda}}_d = \Phi^{-1/3}[\lambda^{-1/2}\underline{\underline{I}} + (\lambda - \lambda^{-1/2})\underline{x}\,\underline{x}], \quad (2)$$

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

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

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

The $\sin^2$ term gives the director anchoring to the network. For small rotations, ω, relative to the matrix it gives the $D_1\omega^2$ term of the de Gennes continuum mechanics approach [7,8]. 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, $\tilde{D}_1$, is related to that before swelling D_1:

$$\tilde{D}_1 = \frac{\Phi^{1/3}}{\lambda}D_1; \qquad D_1 = \frac{(r-1)^2}{r}Y_o; \quad (4)$$

with the chain density defined as $n_n = \frac{N}{V_o}$, 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 [9], F_f, we retain only twist,

$$\frac{2\Phi}{V_o K_2}F_f = (\underline{n}\cdot\nabla\times\underline{n} + q)^2 \equiv (-d\theta/dx + q)^2. \quad (5)$$

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,

$$q = \frac{\Phi^{1/3}}{\lambda} q_o - q_s(2\phi - 1). \qquad (6)$$

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, $\tilde{D}_1 q^2$, or the Frank, K_2, energy prevails. This balance is quantified by $\tilde{\alpha}$, the geometric ratio of the two energy scales:

$$\tilde{\alpha} = \sqrt{K_2/\tilde{D}_1}\, q = \frac{\sqrt{\lambda}\, q}{\Phi^{1/6} q_o}\, \alpha_o; \qquad \alpha_o = \sqrt{K_2/D_1}\, q_o\,.$$

In Ref. [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 optimize over θ profiles to find the minimal free energy, and some untwisting occurs (the efficiency of imprinting is <1; see Fig. 1).

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

The mixing free energy density can be written as

$$f_m = n_m k_B T[\chi_{lr}\phi(1 - \phi)(1 - \Phi)^2 + \phi(1 - \Phi)\ln\phi + (1 - \phi)(1 - \Phi)\ln(1 - \phi) + (1 - \Phi)\ln(1 - \Phi)$$
$$+ \chi_{ln}\phi(1 - \Phi)\Phi + \chi_{rn}(1 - \phi)(1 - \Phi)\Phi], \qquad (7)$$

where $n_m = 1/v_m$ is the solvent number density (with v_m the volume occupied by a single solvent molecule). The usual χ 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

$$F = NF_n + F_f + \frac{V_o}{\Phi} f_m. \qquad (8)$$

As in the case of imprinting, we need to minimize energy over the profile of nematic director orientation θ as we go down the pitch axis. We can do this first since the mixing part does not contain θ, and then we need to find the optimal λ. 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
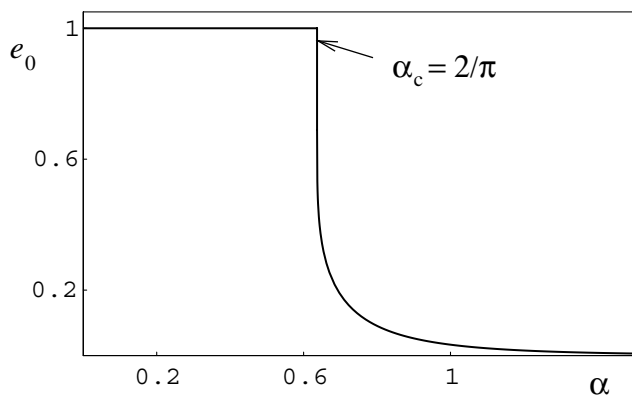

FIG. 1. Imprinting efficiency vs network parameter α. The slope at the critical point $\alpha = \alpha_c^+$ diverges.

is no D_1 penalty, but a Frank penalty for not having the currently desired twist q:

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

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

$$-K_2 \frac{qq_o}{\lambda^2} + Y_o\left(\lambda - \frac{1}{\lambda^2}\right) = 0. \qquad (9)$$

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

$$\epsilon \approx -\frac{K_2}{Y_o}[\phi^{1/3} q_o - q_s(2\phi - 1)]q_o. \qquad (10)$$

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 ϵ ($\sim 10^{-3}$) applies to most materials. Note that the explicit Φ dependence has vanished in this limit, and the shape relaxation is independent of the degree of swelling except indirectly through ϕ. Substituting $\lambda \approx 1$ back, we have

$$f(\phi) = \frac{K_2}{2} \tilde{q}^2 + \frac{3\Phi^{1/3}}{2} Y_o + f_m, \qquad (11)$$

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

$$\frac{\Delta\mu}{k_B T} = \eta + \chi_{lr}(1 - 2\phi)(1 - \Phi) + \ln\frac{\phi}{1 - \phi},$$

where $\eta = -2K_2 \tilde{q} q_s/[n_m k_B T(1 - \Phi)]$. In the reservoir (no network, $\Phi \to 0$, $\phi_l \to \phi_o$, and $\phi_r \to 1 - \phi_o$), the mixing energy density f_r is
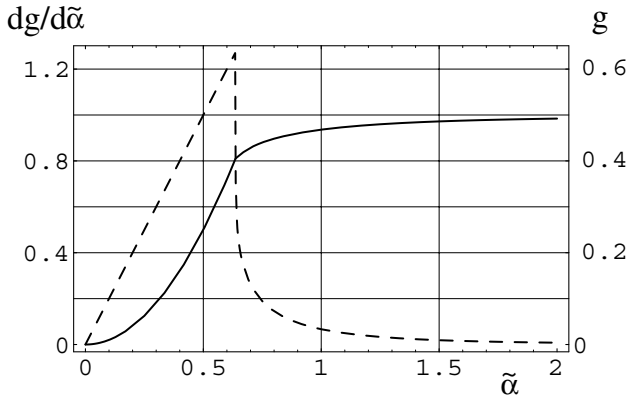
FIG. 2. Director profile free energy $g(\tilde{\alpha})$ and derivative $dg(\tilde{\alpha})/d\tilde{\alpha}$ (dashed line) against imprinting power $\tilde{\alpha}$.

$$\frac{f_r}{n_m k_B T} = \chi_{lr}\phi_o(1 - \phi_o) + \phi_o \ln\phi_o$$
$$+ (1 - \phi_o)\ln(1 - \phi_o),$$

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:

$$\chi_{lr}(1 - 2\phi_o) + \ln\frac{\phi_o}{1 - \phi_o} = \eta + \chi_{lr}(1 - 2\phi)$$

$$\times (1 - \Phi) + \ln\frac{\phi}{1 - \phi}. \tag{12}$$

Suppose the χ_{lr} terms are negligible and that $K_2\tilde{q}q_s \ll n_m k_B T$; i.e., η is small compared to 1. We then have for the l concentration, ϕ, in the network, given ϕ_o in the reservoir,

$$\phi \approx \frac{1 - \eta}{1 - \eta\phi_o}\phi_o. \tag{13}$$

We should also equate the osmotic pressures $(\partial F/\partial\Phi)$ to determine the equilibrium values of Φ, in addition to the ϕ obtained above. In practice, Φ 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:

$$f(\phi, \lambda) = F\Phi/V_o = \frac{\tilde{D}_1}{4} + \frac{\Phi^{1/3}}{2}Y_o\left(\lambda^2 + \frac{2}{\lambda}\right) + f_m.$$

Minimization over λ yields $\tilde{\lambda} = [(r + 1)^2/4r]^{1/3}$ and the free energy

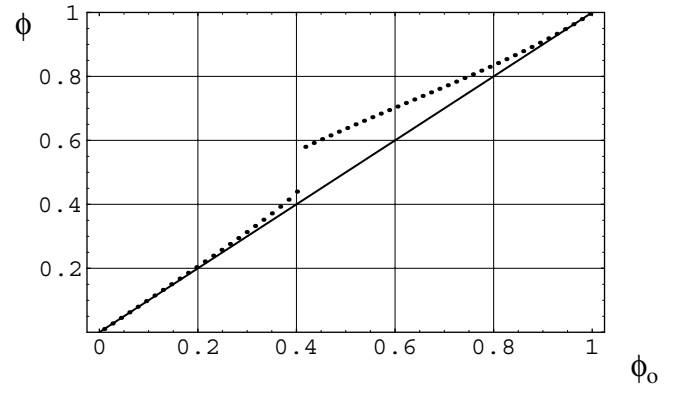$$f(\phi) = \frac{3\Phi^{1/3}Y_o}{2}\left[\frac{(r + 1)^2}{4r}\right]^{2/3} + f_m, \tag{14}$$

FIG. 3. Chiral demixing in the network, ϕ, against reservoir solvent handedness, ϕ_o. See text for parameters used.

from which it follows that

$$\frac{\Delta\mu}{k_B T} = \chi_{lr}(1 - 2\phi)(1 - \Phi) + \ln\frac{\phi}{1 - \phi}.$$

Equating the chemical potential difference to $\Delta\mu_r$ leads to the equilibrium value of ϕ. If we assume that the χ_{lr} term is small so that χ_{lr}^2 and higher order terms in χ_{lr} can be ignored, then the network ϕ is close to that, ϕ_o, in the reservoir:

$$\phi/\phi_o \approx 1 + \chi_{lr}(1 - 2\phi_o)(1 - \phi_o)\Phi. \tag{15}$$

The intermediate $\tilde{\alpha}$ regime.— In general, minimization over the θ profile [3] gives

$$f(\phi, \lambda) = g(\tilde{\alpha})\tilde{D}_1/2 + \frac{\Phi^{1/3}}{2}Y_o\left(\lambda^2 + \frac{2}{\lambda}\right) + f_m \tag{16}$$

with the profile free energy $g(\tilde{\alpha})$ given by

$$g(\tilde{\alpha}) = \tilde{\alpha}^2 \qquad\qquad \text{for } \tilde{\alpha} < 2/\pi,$$
$$= \tilde{\alpha}^2 - k^{-2} + 1 \quad \text{for } \tilde{\alpha} > 2/\pi, \tag{17}$$

and where k is related to $\tilde{\alpha}$ via $\tilde{\alpha} = 2\mathcal{E}(k)/\pi k$ (see Fig. 2 for g and its derivative). $\mathcal{E}$ is the complete elliptic integral of the second kind. Minimization of $f(\phi, \lambda)$ over λ gives a condition for the optimum $\lambda = \tilde{\lambda}$,

$$\left[\frac{\partial g}{\partial\tilde{\alpha}}\frac{\partial\tilde{\alpha}}{\partial\lambda} - \frac{g}{\lambda}\right]\frac{(r - 1)^2}{2\lambda r} + \left(\lambda - \frac{1}{\lambda^2}\right) = 0. \tag{18}$$

Equating the network and reservoir exchange chemical potentials yields

$$-\gamma\frac{\partial g}{\partial\tilde{\alpha}} + \frac{1}{n_m k_B T}\frac{1}{1 - \Phi}\frac{\partial f_m}{\partial\phi} = \frac{1}{n_m k_B T}\frac{\partial f_r}{\partial\phi_o}, \tag{19}$$

where the prefactor γ is given by

$$\gamma = \frac{(r - 1)^2}{r}\frac{n_n}{n_m}\frac{\Phi^{1/6}}{1 - \Phi}\frac{q_s}{q_o}\frac{\alpha_o}{\tilde{\lambda}^{1/2}}.$$

Substituting the expressions for f_m and f_r leads to

$$-\gamma\frac{\partial g}{\partial\tilde{\alpha}} + \chi_{lr}(1 - 2\phi)(1 - \Phi) + \ln\frac{\phi}{1 - \phi} = \chi_{lr}(1 - 2\phi_o) + \ln\frac{\phi_o}{1 - \phi_o}. \tag{20}$$
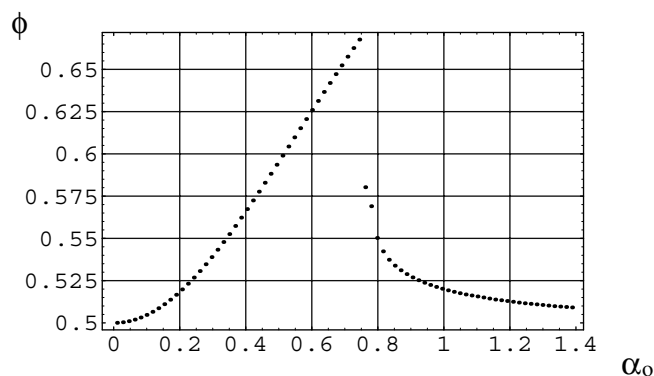
FIG. 4.   Demixing, ϕ, versus formation imprinting power, α_o, with constant reservoir concentration $\phi_o = 0.5$.

FIG. 5.   Demixing dependence on χ_{lr}, ϕ, versus reservoir ϕ_o for $\chi_{lr} = 0$, 0.5 (dashed line), 1 (dotted line).

The first term on the left hand side of the equation is the contribution from the solvent-network interaction, which discriminates between the solvent handedness. If γ and Φ tend to zero, we recover the situation where $\phi = \phi_o$.

Assuming that Φ and $\tilde{\lambda}$ do not depend sensitively on $\tilde{\alpha}$ (which seems justified by the independence of $\tilde{\lambda}$ on $\tilde{\alpha}$ in both the small and large $\tilde{\alpha}$ limits), we can solve Eq. (19) by approximating $\tilde{\lambda} \approx 1$ and taking a set of typical illustrative parameters: $\Phi = 0.9$, $\alpha_o = 2/\pi$, $r = 2$, $n_n/n_m = 0.2$, $q_s/q_o = 1$, and $\chi_{lr} = 0$. The solution is shown in Fig. 3.

Figure 3 shows that $\phi > \phi_o$ is generally satisfied: the solvent handedness which agrees with the network is favored 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, α_o, we can see from Fig. 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 χ_{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 Fig. 5 that a positive value of $\chi_{lr}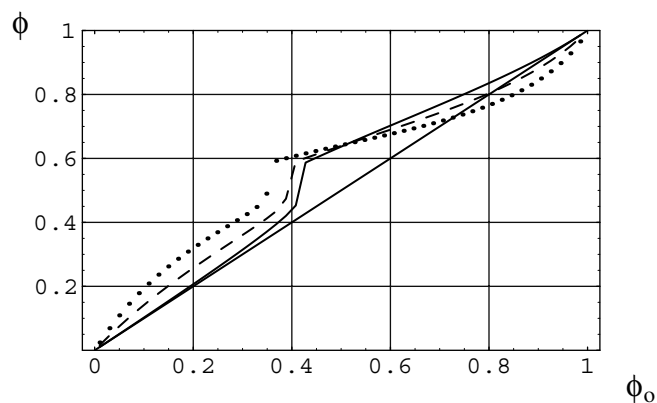$ favors demixing at small ϕ_o. Repeated cycles of our chiral pump will push ϕ to the intersection of the curve with the line $\phi = \phi_o$.

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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