Many types of soft condensed matter exhibit chiral order on the macroscopic length scale. In some materials, macroscopic chiral order is a direct consequence of molecular chirality. For example, in cholesteric liquid crystals, the packing of neighboring chiral molecules leads to a large-scale helical twist of the molecular orientation $\mathbf{n}$ $\times$ $\mathbf{b}$. However, in other materials, the relationship between molecular chirality and macroscopic chiral order is more complex. Some liquid crystals develop chiral order through a spontaneous symmetry-breaking transition, although they are composed of achiral molecules $\mathbf{a}$ $\mathbf{b}$. Likewise, some polymers amplify slight chiral perturbations to give highly ordered helical chains $\mathbf{a}$. In recent experiments, Nakata et al. have found a novel relationship between molecular chirality and macroscopic chiral order in a bent-core liquid crystal $\mathbf{f}$. This material forms a smectic phase with layers of alternating right- and left-handed chirality, which we call “antichiral” order, in spite of the fact that it is composed of uniformly chiral molecules, i.e. 100% of a single enantiomer. In this paper, we develop a theory to explain how antichiral order can occur in systems of chiral molecules. We predict a phase diagram with a second-order transition between antichiral order and homogeneous chiral order, and discuss how this phase diagram can be explored in further experiments on bent-core liquid crystals.

Bent-core liquid crystals can have different types of order from layer to layer. As shown in Fig. 1(b-c), adjacent smectic layers can be synclinic (same tilt) or antiferroelectric (opposite tilt). Likewise, adjacent layers can be ferroelectric (same $\mathbf{b}$) or antiferroelectric (opposite $\mathbf{b}$). If layers are synclinic and ferroelectric, or if they are antiferroelectric and antiferroelectric, then they have the same layer chirality $\chi$. In this case, the bulk liquid crystal is homogeneously chiral. By contrast, if layers are synclinic and antiferroelectric, or if they are antiferroelectric and ferroelectric, then they have the opposite layer chirality $\chi$. In that case, the bulk liquid crystal has an alternating chiral structure. This alternating structure has been called a “racemic” structure by Link et al. $\mathbf{g}$. However, we propose the more specific term “antichiral” to emphasize that there is a rigid alternation between right- and left-handed layers, rather than just a 50/50 statistical distribution of right- and left-handed domains. The term “antichiral” has been used to describe the packing...
of right- and left-handed helices in crystals of polypropylene \[11\], and our usage is consistent with that literature.

If a bent-core liquid crystal is composed of achiral molecules, the right- and left-handed layer structures are exact mirror images of each other, and hence they have the same free energy. For that reason, they should occur equally often. By contrast, if a bent-core liquid crystal is composed of chiral molecules, the molecular chirality breaks the symmetry between right- and left-handed layer chirality. In other words, the right- and left-handed layers become diastereomers rather than enantiomers. Hence, they do not have the same free energy, so one structure is energetically preferred compared to the other. Indeed, adding a low concentration of a chiral dopant to an achiral bent-core liquid crystal converts most of the liquid crystal to a homogeneously chiral state of a single handedness \[9\]. However, Nakata et al. made a surprising discovery: In experiments on well-aligned domains of the chiral bent-core liquid crystal 8OPIMB6*, they found a smectic phase that was both antclinic and ferroelectric \[6\]. This result was consistent with earlier studies of unaligned cells of the same material \[12\]. This combination of tilt and polar order implies that the smectic layers are antichiral. Hence, the phase has alternating right- and left-handed layers, even though the chirality of the molecules must favor one sense of the layer chirality.

The experiment of Nakata et al. leads to an important theoretical issue: What is the relationship between molecular chirality and macroscopic chiral order in a bent-core liquid crystal? In particular, how can the macroscopic order be antichiral when the molecules are uniformly chiral? The macroscopic chiral order should respond in some way to the molecular chirality. We would like to develop a theory for this relationship.

To address this issue, we map the system of bent-core liquid crystals onto the antiferromagnetic Ising model in a uniform magnetic field \[13\]. The Hamiltonian is

\[
H = +J \sum_i \sigma_i \sigma_{i+1} - h \sum_i \sigma_i \label{eq:hamiltonian}
\]

In this mapping, the Ising spin \(\sigma_i\) represents the chiral order \(2(\hat{a} \times \hat{n}) \cdot \mathbf{B}(\hat{a} \cdot \hat{n})\) of layer \(i\). Hence, \(\langle \sigma_i \rangle = +1\) corresponds to an ideal right-handed layer and \(\langle \sigma_i \rangle = -1\) to an ideal left-handed layer. A fractional value of \(\langle \sigma_i \rangle\) corresponds either to reduced uniform chiral order in the layer (e.g. a reduced value of the tilt) or to an average over coexisting regions of different chiral order. The Ising field \(h\) represents the uniform chirality of the molecules, which favors one sense of the layer chirality. The Ising exchange constant \(J\) represents the interaction between adjacent layers. This constant is positive, so that the layer interfaces tend to be antichiral (e.g. antinamic and ferroelectric). This preference for antichirality presumably arises from steric interactions between molecular tails at the layer interfaces.

There is a competition between the two terms in the Hamiltonian: the \(h\) term favors homogeneous chiral order, with the handedness favored by the sign of \(h\), while the \(J\) term favors an alternation from layer to layer. Hence, we need to solve the model to determine whether the layers are homogeneous or alternating for particular values of \(h\) and \(J\).

To solve this model, we use mean-field theory. We suppose that each layer responds to the mean field due to the adjacent layers at the temperature \(T\). We look for a solution with alternating layers

\[
\langle \sigma_i \rangle = \begin{cases} 
\chi_1 & \text{if } i \text{ is odd}, \\
\chi_2 & \text{if } i \text{ is even}.
\end{cases}
\]

\[
\chi_1 = \tanh \left( \frac{-2J\chi_2 + h}{k_B T} \right)
\]

\[\chi_2 = \tanh \left( \frac{-2J\chi_1 + h}{k_B T} \right)\]

FIG. 2: Numerical solution for the chiral order parameters of the odd and even layers, \(\chi_1\) and \(\chi_2\), as functions of the molecular chirality \(h\), for three values of the interlayer interaction \(J\). (a) \(J/k_B T = 0.6\). (b) \(J/k_B T = 0.7\). (c) \(J/k_B T = 0.8\). There is a second-order transition between antichiral order and homogeneous chiral order at a critical value of \(h\), which increases as a function of \(J\).
the chiral-antichiral transition depends on $J$, the interlayer interaction, or the temperature $T$.

$$\chi_2 = \tanh \left( \frac{-2J\chi_1 + h}{k_BT} \right).$$  \hspace{1cm} (3b)

These equations must be solved self-consistently to obtain $\chi_1$ and $\chi_2$ as functions of $h/k_BT$ and $J/k_BT$.

The numerical solution of the mean-field equations is shown in Fig. 2. When the molecular chirality $h = 0$, the layer order parameters $\chi_1$ and $\chi_2$ have equal and opposite values, indicating that odd and even layers are mirror images of each other. In that case, the system has perfect antichiral order. As $h$ increases, the positive order parameter $\chi_1$ becomes slightly larger, and the negative order parameter $\chi_2$ becomes less negative. Still, there is an alternation between odd and even layers with right- and left-handed chiral order, and hence the system is still antichiral. This alternating layer structure persists up to a critical value of $h$, where there is a second-order transition to homogeneously chiral layers, with the same value of $\chi$. Beyond that transition, the chiral order parameter of the layers increases smoothly as a function of $h$.

A three-dimensional plot of $\chi_1$ and $\chi_2$ as functions of $h/k_BT$ and $J/k_BT$ is presented in Fig. 3. This plot shows that the antichiral state is favored for large $J$ and small $h$, while the homogeneously chiral state is favored for large $h$ and small $J$. Moreover, the plot shows that the second-order transition can be driven by varying the molecular chirality $h$, the interlayer interaction $J$, or the temperature $T$. Increasing $J$ breaks the symmetry between the layers, while increasing $h$ or $T$ restores the symmetry. Thus, the transition shown in Fig. 2 for varying $h$ is continuously connected to the standard Ising antiferromagnetic transition for varying $T$ at $h = 0$.

In Figs. 2 and 3, we see that the critical value of $h$ for the chiral-antichiral transition depends on $J$. As $J$ increases, the alternating layer structure persists to higher values of $h$. To find the critical value $h_c$ as a function of $J$, we look for a solution of the mean-field equations \([4]\) with the layer order parameters $\chi_{1,2} = \chi_c \pm \delta\chi$. As we approach the transition, we have $\delta\chi \to 0$, and hence the mean-field equations require

$$\chi_c = \tanh \left( \frac{-2J\chi_c + h}{k_BT} \right),$$  \hspace{1cm} (4a)

$$\delta\chi = \frac{2J\delta\chi}{k_BT} \text{sech}^2 \left( \frac{-2J\chi_c + h}{k_BT} \right).$$  \hspace{1cm} (4b)

The solution of these equations is

$$\chi_c = \sqrt{1 - \frac{k_BT}{2J}},$$  \hspace{1cm} (5a)

$$h_c = \frac{2J}{k_BT} \sqrt{1 - \frac{k_BT}{2J}} + \tanh^{-1} \frac{1 - \frac{k_BT}{2J}}{2J}. \hspace{1cm} (5b)$$

Equation \((5b)\) gives the phase boundary between the antichiral state and the homogeneously chiral state. This boundary is plotted in the phase diagram of Fig. 4.

So far, the experiments of Nakata et al. \([7]\) have studied the antichiral state in the single chiral bent-core liquid crystal SOPIMB6*. In this compound, the chiral centers are located near the ends of the flexible hydrocarbon chains, far from the bent core of the molecule. For that reason, the chiral centers should only have a small effect on the relative energies of the right- and left-handed layer structures. In other words, for these molecules, the parameter $h$ should be low. By contrast, the parameter $J$ arises from the interfacial energy of adjacent smectic layers, which tend to be antclinic and ferroelectric, and hence $J$ should be substantial. The regime of small $h$ and large $J$ is consistent with the antichiral state in the theoretical phase diagram.

To map out the rest of the phase diagram, future experiments will need to vary $h$ and $J$. The molecular chi-
rality parameter $h$ can be changed either through chemical synthesis or through doping experiments. For the synthetic approach, one would prepare molecules analogous to SOPIMB6*, but with the chiral centers closer to the bent core. By synthesizing a series of molecules with the chiral centers in different positions, one could gradually increase $h$. Alternatively, one could dope SOPIMB6* with varying concentrations of a chiral dopant—perhaps another bent-core liquid crystal that forms a homogeneously chiral state. Increasing the dopant concentration should gradually increase $h$. The doping approach should actually increase $h$ in a more quantitatively controllable way than the synthetic route, as long as the compounds do not phase separate. In either case, we would expect to see a transition from the antichiral state to the homogeneously chiral state as $h$ increases.

Changing the interlayer interaction $J$ will require changes in the layer interfaces. In particular, to explore the theoretical phase diagram, one will need to reduce the energetic preference for anticlinic and ferroelectric packing of adjacent layers. Hence, one should partially decouple the layers. This might be done by doping SOPIMB6* with molecules that segregate into the interstices between the layers (analogous to the naphthaphase segregation seen in simulations by Maiti et al. [14]). The parameter $J$ would then be a continuously decreasing function of dopant concentration. We would expect to see a transition from antichiral to homogeneously chiral as more dopant is added and the layers become more decoupled.

As a final point, our predictions for bent-core liquid crystals can be compared with chiral ordering in polymers. There have been several experimental and theoretical studies of chiral ordering in polyisocyanates. In these materials, steric constraints force the polymer main chain to have a helical structure, which can be either right- or left-handed. The handedness of the helix is determined by slight chiral perturbations, such as chiral centers in the monomers. For example, copolymers of right- and left-handed units have been called “majority-rule” copolymers, because they follow whichever chiral units are in the majority. Likewise, copolymers of chiral and achiral units have been called “sergeants-and-soldiers” copolymers, because the achiral “soldiers” follow the helical sense selected by the chiral “sergeants.”

This chiral ordering has been explained theoretically by a mapping onto the Ising model [15, 16].

In both polyisocyanates and bent-core liquid crystals, the chiral order of the large-scale structure is a complex collective phenomenon. In both cases, a theory based on the Ising model can explain the nonlinear relationship between molecular chirality and macroscopic chiral order. However, there is one important difference between polyisocyanates and bent-core liquid crystals. In polyisocyanates, the interaction between neighboring units along the polymer favors uniform helicity. For that reason, polyisocyanates respond sensitively to slight chiral perturbations. By contrast, in the bent-core liquid crystal SOPIMB6*, the interaction between adjacent smectic layers favors alternating layer chirality. Hence, these materials resist uniform chiral order, and respond insensitively to molecular chirality. For that reason, they might be called a “sergeants-and-students” system.

In conclusion, we have developed a theory for antichiral order in bent-core liquid crystals. This theory explains the surprising experimental discovery that antichiral order can occur even in systems of uniformly chiral molecules. It predicts a phase diagram for the antichiral state and the homogeneously chiral state, which can be explored in future experiments.

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[1] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, 2nd ed. (Oxford University Press, Oxford, 1993).
[2] A. B. Harris, R. D. Kamien and T. C. Lubensky, Rev. Mod. Phys. 71, 1745 (1999).
[3] R. D. Kamien and J. V. Selinger, J. Phys.: Condens. Matter 13, R1 (2001).
[4] J. V. Selinger, Z.-G. Wang, R. F. Bruinsma, and C. M. Knobler, Phys. Rev. Lett. 70, 1139 (1993).
[5] J. Pang and N. A. Clark, Phys. Rev. Lett. 73, 2332 (1994).
[6] M. M. Green, J. W. Park, T. Sato, A. Teramoto, S. Lifson, R. L. B. Selinger, and J. V. Selinger, Angew. Chem. Int. Ed. 38, 3139 (1999).
[7] M. Nakata, D. R. Link, F. Araoka, J. Thisayukta, Y. Takanishii, K. Ishikawa, J. Watanabe, and H. Takezoe, Liquid Crystals 28, 1301 (2001).
[8] T. Niori, T. Sekine, J. Watanabe, T. Furukawa, and H. Takezoe, J. Mater. Chem. 6, 1231 (1996).
[9] D. R. Link, G. Natale, R. Shao, J. E. Maclennan, N. A. Clark, E. Körblová, and D. M. Walba, Science 278, 1924 (1997).
[10] J. Xu, R. L. B. Selinger, J. V. Selinger, and R. Shashidhar, J. Chem. Phys. 115, 4333 (2001). The definition of $\chi$ in that paper differs by a factor of 2 from the definition here.
[11] B. Lotz, J. C. Wittmann, and A. J. Lovinger, Polymer 37, 4979 (1996).
[12] E. Gorecka et al., Phys. Rev. E 62, R4524 (2000).
[13] D. A. Lavis and G. M. Bell, *Statistical Mechanics of Lattice Systems*, 2nd ed. (Springer, Berlin, 1999), Vol. 1, Chap. 4.
[14] P. K. Maiti, Y. Lansac, M. A. Glaser, and N. A. Clark, Phys. Rev. Lett. 88, 065504 (2002).
[15] J. V. Selinger and R. L. B. Selinger, Phys. Rev. Lett. 76, 58 (1996).
[16] J. V. Selinger and R. L. B. Selinger, Phys. Rev. E 55, 1728 (1997).