I. INTRODUCTION

A remarkable property of many liquid crystal (LC) phases is that chirality at the molecular level can be transmitted to the phase itself. For example, instead of forming a nematic LC, chiral molecules will form a chiral nematic (or cholesteric phase) in which the liquid crystal director undergoes a helical twist. Similarly, if a nematic is doped with a small amount of chiral solute, then the whole phase becomes chiral. Enantiomers of a chiral solute are known to induce an equal but opposite twist in the host phase. Here the different handedness of helical twist is determined by chiral intermolecular interactions between the enantiomers and the liquid crystal solvent. The degree of twist induced can vary greatly between different solutes. A quantitative measure is provided by the macroscopic helical twisting power (HTP)

\[ \beta_M = (Pc_v r)^{-1}, \]

where \( P \) is the helical pitch of the phase induced by the dopant, \( c_v \) is the weight concentration of chiral dopant and \( r \) is the enantiomeric purity of the phase.

There are a number of important uses for chiral dopants in liquid crystal applications. Of particular importance is their use in twisted nematic displays, where a small amount of dopant can ensure a uniform direction to the twist in an LC cell. Moreover, a small quantity of chiral solute can be added to a nematic liquid crystal polymer prior to initiation of a cross-linking reaction. In this way, chiral polymer films can be made, which prove useful in improving the viewing angle of displays or can be used as thermally controllable reflective polarizers. The desire to limit other effects of the chiral molecule (such as detrimental effects on elastic constants, dielectric anisotropy, rotational viscosity or induced demixing in a display mixture) and the limited solubility of many dopants means that there is considerable interest in designing molecules with high HTP values (>100 \( \mu \)m\(^{-1}\)). In this case, a small quantity of chiral dopant can impart a helical twist without spoiling the other carefully optimized material properties of the host system.

Considerable progress has been made in predicting helical twisting powers. Surprisingly, methods based on single molecule studies work well. The theory of Nordio, Ferrarini and co-workers has had considerable success in predicting the helical twisting power of rigid dopants where the molecular conformation can be predicted by molecular or quantum mechanical means, and simple flexible dopants where a small number of well-defined conformations are possible. Recently, the current authors have extended this model to treat flexible dopants using a Monte Carlo simulation approach. It is clear from the latter that each individual conformation of a flexible dopant can have a different magnitude for its HTP. Moreover, different conformations of the same molecule can have positive or negative HTPs. The distribution of conformations is therefore of fundamental importance in determining the overall HTP of a flexible dopant. Conformational changes induced by changes in temperature can therefore be used to explain the temperature dependence of HTP values and even the helical twist inversion in cholesteric phases. Recently, an alternative single molecule technique has been derived. Initial results indicate that this is equally successful in predicting both the sign and magnitude of HTPs across a series of rigid chiral dopants.

If intermolecular forces are responsible for the transfer of chirality from solute to host liquid crystal, it becomes an interesting question as to what role the host solvent has in determining the value of the HTP. In many cases the HTP for a chiral solute changes little for measurements taken in similar types of liquid crystal solvent. Here, it seems likely that the most important property of the solvent is the twist elastic constant, \( K_2 \). The latter is fairly similar for many commercial mixtures in which HTP values are measured. (A high value of \( K_2 \) would be expected to reduce the measured HTP.) This explains the surprising success of single-molecule techniques in predicting HTPs for a variety of different molecules measured in similar solvents. However, this is not the full story. In a limited number of studies, the solvent has been shown to be of utmost importance. In these studies changes...
in the polarity of the solvent can change both the magnitude and the sign of HTP. Here it seems likely that the solvent has a major role to play in preferentially selecting certain conformations. Changes in solvent polarity, cause changes in the preferred conformations of the solute and therefore induce major changes in the measured HTP.19

Unfortunately, it is difficult to properly examine the role played by the solvent in determining HTP values using theoretical methods. In principle, the route to this is well defined.20,21 An enantiomer immersed in a twisted nematic solvent, which wants to twist in the same direction as the solvent, will have a lower free energy than its mirror image molecule. Accurate measurement of the free energy difference between the two solute/solvent systems will therefore provide a route to the HTP.20,21 This has been attempted recently for a number of rigid dopants by Wilson and co-workers in Gay–Berne22 and spherocylinder23 solvents. However, the free-energy differences are small (less than 1 kJ mol\(^{-1}\)) making this a difficult route for the determination of HTP values. An alternative has been suggested by the recent work of Germano et al.24 In this study, the helical pitch of a chiral form of the Gay–Berne potential25 was predicted based on calculations of the torque density during simulations of the liquid crystal phase. For real chiral dopants, it should therefore be possible to measure the torque induced in a solvent system by the presence of the chiral dopant. The latter could provide an alternative route to HTPs, and allow for the assessment of the role played by different solvents.

In the current paper, we examine the practicalities of using the torque density as a route to HTPs. We present calculations for the torque density in systems of achiral liquid crystalline particles that are doped with a single chiral molecule, and the results are related to the HTPs of the chiral dopants. The structure of the paper is as follows: the theory behind the method is described in Sec. II, the computational model and the simulation details are given in Sec. III, the results are presented and discussed in Sec. IV, and in Sec. V we draw our conclusions.

II. THEORY

Following Germano et al.,24 one can define the total potential energy of a system as \( U_\lambda \), so that it depends on a chirality parameter, \( \lambda \). An achiral system has \( \lambda = 0 \) and enantiomeric systems have opposite signs of \( \lambda \). The equilibrium pitch wave number of a system can similarly be defined as

\[
q_\lambda = \frac{2\pi}{\lambda_0},
\]

where \( \lambda_0 \) is the number density of dopant molecules. Now, following Allen,20 if a uniformly twisted nematic with a wave vector \( k = 2\pi/P \), is doped with small numbers of chiral dopants \( \pm \) then the elastic contribution to the free energy arising from distortions to the uniformly twisted state is

\[
F_{k,\lambda} = \frac{1}{2} N_+ (k-q_\lambda)^2 - (k+q_\lambda)^2
\]

(5)

where \( K_2 \) is the twist elastic constant. We note that Eq. (5) is valid only for small deviations of \( k \) from \( q_\lambda \), where the chiral dopant concentration is of the order of a few percent. The free energy difference between enantiomeric phases with equilibrium pitch wave numbers \( q_{\lambda} = \pm q_\lambda \) is

\[
\Delta F_{k,\pm \lambda} = F_{k,\lambda} - F_{k, -\lambda} = \frac{1}{2} N_+ ((k-q_\lambda)^2 - (k+q_\lambda)^2)
\]

(6)

\[
= -2 N_+ K_2 q_\lambda^2.
\]

This expression is evaluated in Refs. 22 and 23 using thermodynamic perturbation theory to calculate the helical twisting powers (HTPs) of chiral dopant molecules, where \( k \) is the wave vector imposed on the system by twisted periodic boundary conditions.27

An alternative method can also be used to calculate \( q_\lambda \), and hence \( \beta \), that is based on intermolecular torques. Following de Gennes26 and Allen and Masters,27,28 the free energy density gives rise to a torque density in the system, and the torque per unit area can be expressed microscopically as

\[
\frac{\partial F_{k,\lambda}}{\partial k} = \langle \Pi_{zz} \rangle_{k,\lambda},
\]

(7)

where the helical axis is chosen along the \( z \) axis and the tensor \( \Pi_{\alpha\beta} \) is defined as

\[
\Pi_{\alpha\beta} = \frac{1}{2} \sum_r \frac{r_{ij} \tau_{ij\beta}}{\beta} = \frac{1}{2} \sum_{ij} \frac{r_{ij} \tau_{ij\beta}}{\beta}
\]

(8)

where \( \alpha, \beta = x, y, z \); \( r_{ij} = r_i - r_j \) is the \( \alpha \) component of the center of mass separation of particles \( i \) and \( j \), and \( \tau_{ij\beta} \) is the \( \beta \) component of the torque exerted by particle \( j \) on particle \( i \). Following Germano et al.24 comparison of Eq. (7) and the macroscopic expression

\[
\frac{1}{V} \frac{\partial}{\partial k} F_{k,\lambda} = K_2 (k-q_\lambda),
\]

(9)

leads to

\[
\langle \Pi_{zz} \rangle_{k,\lambda} = K_2 q_\lambda = h_\lambda,
\]

(10)

for the case where \( k = 0 \) and

\[
\langle \Pi_{zz} \rangle_{k,\lambda} = K_2 q_\lambda - k,
\]

(11)

for the case where \( k \neq 0 \). Thus, \( K_2 \) and \( q_\lambda \) can be determined from

\[
\beta \approx \frac{2\beta}{\lambda_0},
\]

(4)

where \( \rho \) is the number density of dopant molecules.
where the solute energy, \(N\), the number of solvent molecules, and \(u^\hat{\mathbf{u}}\) where \(q_i\) between a single atomic site, \(K_2\) in fluids of achiral molecules. However, the quantity of interest in this study is the HTP, \(\beta_M\), that is directly proportional to \(q_s\). From Eq. (10), a single simulation of a chiral molecule in an untwisted nematic \((k=0)\) will yield \(K_2\), which is directly proportional to \(q_s\). If we know the value of \(K_2\) this provides a route to calculating \(\beta_M\) by combining Eqs. (3), (4), and (10),

\[
\beta_M = \frac{2q_s}{4\pi c_w} = \frac{2\langle \Pi_{zz} \rangle_{0,k}}{4\pi c_w V K_2}. 
\]

### III. COMPUTATIONAL AND SIMULATION DETAILS

In this paper we use Eq. (10) to determine the factor \(h_{\lambda}\), and thus \(\beta_M\), by calculating \(\langle \Pi_{zz} \rangle_{0,k}\) from a simulation of a chiral molecule in a nematic solvent.

In this work, a fully atomistic, rigid, energy minimized liquid crystalline solvent in a simulation box subject to periodic boundary conditions. The total energy of the combined solute/solvent system is calculated as

\[
U_{\text{tot}} = U_{\text{solute}}^{\text{MM2}} + \sum_{i=1}^{N_{\text{GB}}} \sum_{j=1}^{N_{\text{GB}}} U_{ij}^{\text{MM2}} + \sum_{i=1}^{N_{\text{atoms}}} \sum_{j=1}^{N_{\text{GB}}} U_{ij}^{\text{MM2/GB}}, 
\]

where the solute energy, \(U_{\text{solute}}^{\text{MM2}}\) is defined as the energy of the chiral dopant molecule in the MM2 force field, \(N_{\text{GB}}\) is the number of solvent molecules, and \(N_{\text{atoms}}\) is the number of atoms in the solute molecule. The solvent is represented by the Gay–Berne (GB) potential

\[
U_{ij}^{\text{GB}} = 4\epsilon_{ij}^{\text{GB}} \left[ (\sigma_{ij}^{\text{GB}} - \sigma_{ij}^{\text{GB}}) \right]^2 + (\sigma_{ij}^{\text{GB}} - \sigma_{ij}^{\text{GB}})^6 , 
\]

where \(\sigma_{ij}^{\text{GB}}\) and \(\sigma_{ij}^{\text{GB}}\) are the unit vectors along the GB molecular axes, \(r_{ij}\) is the separation vector between the centers of mass of two GB particles, and \(\epsilon_{ij}^{\text{GB}}\) are given by Eqs. (2)–(7) of Ref. 31. The form of the Gay–Berne solvent used employed the cut and shifted version of the potential with the parameters \(\kappa = 3, \kappa' = 5, \mu = 2, \nu = 1\). The phase diagram of this system has been studied previously by de Miguel and co-workers. The simulation constants used in Eq. (16) were taken as \(\sigma_0^{\text{GB}} = 5.7\ \text{Å}\), and \(\epsilon_0^{\text{GB}} = 3.325\ 76\ \text{kJ mol}^{-1}\), and a reduced density of \(\rho^* = 0.33\) was used where \(\rho^* = \rho \sigma_0^{\text{GB}}\). The conditions correspond to a stable nematic liquid crystalline phase with an order parameter \(S_2 = 0.7\) at a temperature \(T = 400\ \text{K}\). The solute–solvent interaction energy, \(U_{ij}^{\text{MM2/GB}}\), between a single atomic site, \(i\), in the solute molecule and a solvent molecule, \(j\), takes the form proposed by Cleaver et al.\(^{33}\) that has also been used in studies of hybrid Lennard-Jones–Gay–Berne mesogens.\(^{34,35}\)

\[
U_{ij}^{\text{MM2/GB}} = 4\epsilon_{ij}^{\text{MM2/GB}} \left[ (\sigma_{ij}^{\text{MM2}})^2 + (\sigma_{ij}^{\text{MM2}})^2 \right]^{1/2} 
\]

In Eq. (17), \(\sigma_0^{\text{MM2/GB}} = (\sigma_0^{\text{MM2}})^2 + (\sigma_0^{\text{MM2}})^2 \), where \(\sigma_0^{\text{MM2}}\) and \(\sigma_0^{\text{MM2}}\) values are taken from the \(\epsilon^*\) and van der Waals radii in the MM2 Hill potential. \(\sigma_0^{\text{MM2/GB}}\) and \(\epsilon_0^{\text{MM2/GB}}\) in Eq. (17) are given by

\[
\sigma_0^{\text{MM2/GB}}(\hat{\mathbf{u}}_i, \mathbf{r}_j) = \sigma_0^{\text{MM2/GB}} \left[ 1 - \chi \alpha^2 (\mathbf{r}_j \cdot \mathbf{u}_i) \right]^{1/2} 
\]

where \(\chi\) and \(\chi'\) are given by Eqs. (21) and (38) of Ref. 33, respectively.

\(NVT\) Monte Carlo (MC) simulations were used to study the chiral dopant in a nematic phase composed of 243 solvent molecules. The simulations proceed as follows: the solute molecule is initially gradually grown into the solvent over \(10^5\) MC steps using the method described in Ref. 23 and the system is then equilibrated for \(1.2\times10^5\) MC steps to ensure that the solvent is well ordered around the chiral solute molecule. Production runs of \(1.6\times2.5\times10^5\) MC steps are then performed and the tensor \(\Pi_{zz}\) is calculated (see below) at each step. Averages are calculated over blocks of \(5\times10^5\) MC steps, so that between 32 and 50 independent block averages contribute to the overall \(\langle \Pi_{zz} \rangle\) for each system studied.

\(\Pi_{zz}\) is determined from Eq. (8). The torque between GB particles is calculated as

\[
\tau_{ij} = -\Delta U_{ij} / \Delta e_i, 
\]

where \(-\Delta U_{ij}/\Delta e_i\) is the perpendicular component of the torque acting on particle \(i\) from particle \(j\). The torque on the solute molecule is determined as

\[
\tau_i = \sum_{i=1}^{N_{\text{atoms}}} \mathbf{d}_i \times \mathbf{f}_i, 
\]

where \(\mathbf{d}_i\) is the position of atom \(i\) in relation to the center of mass of the molecule, and \(\mathbf{f}_i\) is the force acting on atom \(i\) that arises from the interactions of all solvent molecules with the chiral dopant.

In order to improve the averaging of \(\Pi_{zz}\), the nematic director is constrained to be perpendicular to the \(z\) axis. Following Germano et al.\(^{24,36}\) the director is constrained to the \(xy\) plane by adding a term proportional to \((Q_x^2 + Q_z^2)\) to the total energy of the system, \(U_{\lambda}\), where \(Q\) is the order tensor given by

\[
Q_{\alpha\beta} = \frac{1}{N} \sum_{i=1}^{N} \left( \frac{3}{2} \hat{e}_{i\alpha} \hat{e}_{i\beta} - 2 \delta_{\alpha\beta} \right), 
\]
where $\hat{e}_i$ is a unit vector along the main molecular axis of solvent particle $i$, $N$ is the number of particles, and $\delta$ is the Kronecker delta function.

Six relatively rigid chiral dopant molecules were chosen as solutes. These were either bridged biaryl or helicene derivatives and their structures are shown in Fig. 1. Molecules D and E are enantiomers. The choice of rigid molecules ensured there were no complications arising from poor conformational sampling. However, the technique is not restricted to rigid molecules. A pure Gay–Berne solvent system containing no chiral dopant was also studied to check that an achiral system has \(\langle \Pi_{zz} \rangle_{0,0} \approx 0\). for each of the dopants in Eq. (14) we consider the relative molecular mass of each Gay–Berne particle to be equal to that of the liquid crystal nematogen 4-n-pentyl-4’-cyanobiphenyl (5CB). We note that the magnitude of the values in Table I do not exactly match the experimental values in all cases, but compared to other predictive methods the agreement with experiment is good. HTP values are solvent dependent and we do not expect the Gay–Berne system to completely reproduce the experimental solvent system exactly. However, the results from this study show that the calculation of intermolecular torques in liquid crystalline systems doped with chiral molecules can be used to predict the handedness of the twist induced by a chiral molecule and can also yield an approximate measure of the magnitude of the twist.

The method is subject to large statistical errors. The size of the error in \(\langle \Pi_{zz} \rangle\) depends critically on the system size and the length of the simulation. The liquid crystalline solvent system must be small enough to allow the chiral molecule to have a measurable impact on the system above the background noise caused by normal fluctuations in \(\Pi_{zz}\). However, the relative size of fluctuations in \(\Pi_{zz}\) are larger for smaller system sizes so the choice of system size used requires careful consideration. The system size used in this study; namely 243 GB solvent particles and one atomistic chiral molecule, was chosen in an attempt to provide the best balance between these factors.

In the previous computational study by Germano et al., systems of 1024 and 2048 chiral GB particles were examined. However, chirality was imparted on all molecules in the study and the strength of the chiral potential used was in most cases one or two orders of magnitude larger than would determine the weight concentration, \(c_w\), for each of the dopants in Eq. (14)

\[
\beta_M = \frac{1}{N} \sum_i \hat{e}_i \cdot \mathbf{q}_i
\]

where \(\mathbf{q}_i\) is the molecular torque on particle \(i\), \(\hat{e}_i\) is a unit vector along the main molecular axis of particle \(i\), and \(N\) is the number of particles. The twist elastic constant for the Gay–Berne system used in this study has previously been determined by Allen et al.\(^{37}\) as \(K_z = 6.96 \times 10^{-12} \text{ J m}^{-1}\). Using Eq. (14) we can thus determine predicted values of $\beta_M$ for the chiral dopants and the results are shown in Table I. To

### IV. RESULTS AND DISCUSSION

The results from the study are shown in Fig. 2 where \(\langle \Pi_{zz} \rangle_{0,0}\) is plotted against the experimental \(\beta_M\). As predicted from Eq. (10), \(\langle \Pi_{zz} \rangle_{0,0}\) is of the opposite sign as the helical twisting power and hence \(q_\perp\). In each case, the correct sign of twist is predicted using the method and there is a trend of higher \(\langle \Pi_{zz} \rangle_{0,0}\) at larger HTP values. The results for the achiral system containing no chiral dopant molecules is also shown in Fig. 2 and, within statistical errors, the system was found to be achiral using the method \(\langle \Pi_{zz} \rangle_{0,0} = -0.18 \pm 1.78 \text{ kJ mol}^{-1} \text{Å}\). The twist elastic constant for the Gay–Berne solvent system used in this study has previously been determined by Allen et al.\(^{37}\) as \(K_z = 6.96 \times 10^{-12} \text{ J m}^{-1}\). Using Eq. (14) we can thus determine predicted values of $\beta_M$ for the chiral dopants and the results are shown in Table I. To

![FIG. 1. Structures of the chiral dopant molecules studied and their experimental helical twisting powers, $\beta_M\).](Image)

![FIG. 2. \(\langle \Pi_{zz} \rangle_{0,0}\) plotted against the experimental $\beta_M$ for the six different chiral dopant molecules from Fig. 1 in a Gay–Berne solvent, and for a purely achiral system ($\beta_M=0 \mu \text{m}^{-1}$).](Image)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\beta_M/\mu \text{m}^{-1}$ (Expt.)</th>
<th>$\beta_M/\mu \text{m}^{-1}$ (Pred.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>+69</td>
<td>+71.8±15.5</td>
</tr>
<tr>
<td>B</td>
<td>-55</td>
<td>-14.2±18.5</td>
</tr>
<tr>
<td>C</td>
<td>+80</td>
<td>+113.0±18.6</td>
</tr>
<tr>
<td>D</td>
<td>-55</td>
<td>-35.0±16.1</td>
</tr>
<tr>
<td>E</td>
<td>+55</td>
<td>+26.2±14.9</td>
</tr>
<tr>
<td>F</td>
<td>-13</td>
<td>-3.8±21.4</td>
</tr>
</tbody>
</table>
be expected for real molecules. For this reason, much shorter simulation runs could be used in the previous study compared to those presented in this paper where only one molecule is chiral ($6 \times 10^5$ MC steps in the previous study compared to $1.6-2.5 \times 10^7$ MC steps in this paper). The long simulation times also explain the relatively large statistical errors in the results presented here.

V. CONCLUSIONS

The method of calculating intermolecular torques in liquid crystalline systems containing chiral dopant molecules has been shown to correctly predict the handedness of twist induced by the chiral molecules and shows a good correlation with the magnitude of the helical twisting power of each of the dopants studied. The general method is extremely flexible and allows for the use of many different system sizes and types. A system that includes several chiral dopant molecules in a generic liquid crystalline solvent of Gay–Berne or soft repulsive spherocylinder particles could be used and would produce a larger, and more measurable twist than the system utilized in this study. However, this would result in an increase in the computational cost caused by simulating additional fully atomistic molecules (electrostatic interactions between molecules would also have to be considered), and care would be required as the equations derived in Sec. II are valid only for low chiral dopant concentrations. The approach could be extended to allow the chiral molecule to change conformations by utilizing the computational methods described in Ref. 39. In addition, the method could also be applied to systems where the liquid crystalline solvent is represented by molecules with atomistic detail. Although these studies would be far too computationally expensive to be considered given the computational power currently available, they may become accessible in the future and would allow studies of solvent dependent helical twisting powers to be undertaken. To provide a reliable quantitative measurement of the helical twisting power for a chiral dopant molecule, the method requires further refinement to improve the statistical error in the results and to find the optimum ratio of chiral dopant molecules to liquid crystalline molecules used in the simulation system.

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36. G. Germano (private communication).