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Simple molecular model for induced cholesteric phases

A. Ferrarini, G. J. Moro,* and P. L. Nordio
Dipartimento di Chimica Fisica, Università di Padova, 2 Via Loredan, 35131 Padova, Italy

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A phenomenological theory for the cholesteric phase induced by a chiral solute in a nematic solvent is derived from (i) the continuum representation of twist deformation of the nematic solvent, and (ii) the surface anchoring energy approximation for the interactions between the solvent and a solute of given shape. This allows a simple explanation of the stabilization of the solvent twist deformation by the interactions with chiral solute. A straightforward statistical elaboration leads to the well known inverse proportionality between the pitch of the cholesteric phase and the solute concentration. The corresponding proportionality coefficient, i.e., the twisting power of the solute, is then related to the asymmetry of the solute shape through a chirality order parameter.

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I. INTRODUCTION

The addition of a chiral solute to a thermotropic liquid crystal in its nematic phase often induces a cholesteric phase with a measurable pitch p [1]. For dilute enough solutions, an inverse proportionality is found between the pitch and the solute concentration c expressed as the ratio between solute and solvent numbers of molecules:

$$1/p=\beta c \ . \tag{1.1}$$

The proportionality parameter β measures the twisting power of the solute, for a given solvent and temperature. On a general ground one expects a correlation between the twisting power and the chirality of the solute and this has motivated the large number of investigations about the dependence of β on the type of solute (see Ref. [1] for a review on experimental works on this subject). A variety of systems have been analyzed in order to elucidate the role of the molecular structure in determining both the size and the sign (i.e., the handedness of the induced cholesteric phase) of the twisting power [1,2]. In spite of the effects attributed to specific solute-solvent interactions, these studies suggest that a major role is played by the molecular shape of the solute.

The comparative analysis of the behavior of different solute molecules is hampered by the lack of a theory able to correlate the cholesteric twist with solute chirality. Some efforts have been dedicated to the generalization of the mean-field theory of nematic to cholesteric phases and induced cholesteric phases by using parameterized forms of two-particle interaction potential [3]. Molecular dynamics simulations have been recently done on model systems of cholesteric phases [4]. Of course one would like to recover the cholesteric pitch from an accurate representation of molecular interactions, but this objective is actually far from being reached.

We shall follow a more phenomenological approach with the aim of correlating in simple terms the twisting power β with the asymmetry of the molecular shape of the solute. It can be done by introducing the following approximations: (i) a continuum representation of the twist distortions of the nematic solvent, and (ii) a representation of solute interactions with the nematic solvent of the type of anchoring energy for macroscopic surfaces. Certainly this oversimplifies the molecular interactions responsible for the cholesteric pitch but, on the other hand, it leads to a straightforward correlation between the twisting power β and the solute shape. The methodological analogy with the Stokes-Einstein theory of diffusion coefficients can be invoked in order to clarify the character of our procedure. Also in this case the physical picture beyond the model is that of a macroscopic solute interacting with the solvent represented like a continuum. In principle such a theory can supply only estimates of diffusion coefficients when solute and solvent have a comparable size, albeit these estimates are surprisingly accurate [5] in the absence of specific interactions like association. Moreover, this method rationalizes in simple terms the influence of the molecular shape on the diffusion coefficient [6].

Our treatment has a similar purpose, even if in a quite different context. The relation between solute shape and twisting power will be the final result of our analysis. In this framework specific solute-solvent interactions will be completely neglected. On the other hand, it seems to us that their influence on the cholesteric pitch can be clearly understood only if a reliable theory about the intrinsic effects of the solute shape is available.

The main features of the model have been anticipated in a short communication [7]. Here we shall present the complete treatment with a detailed discussion of its physical basis.

II. THE MODEL FOR THE FREE ENERGY OF INDUCED CHOLESTERIC PHASES

In a recent work a phenomenological treatment has been proposed for the orientational order of a solute in

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*Author to whom correspondence should be addressed.

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nematic phases [8]. The basic hypothesis was that the orientational order derives from the cumulative effects of interactions between the nematic field and each surface element of the solute. A surface S enclosing the excluded volume to be determined, for example, from atomic van der Waals radii, is assigned to each solute. Then, for each orientation Ω of the solute, a pseudopotential $U(\Omega)$ is derived by integrating on the surface S the elementary contributions given by the second Legendre polynomial $P_2(\mathbf{d}\cdot\mathbf{s})$ for the cosine of the angle between the nematic director $\mathbf{d}$ and the unit vector $\mathbf{s}$ orthogonal to a surface element dS:

$$U(\Omega)=\epsilon_{\rm an}\int_S dS[3(\mathbf{d}\cdot\mathbf{s})^2-1]/2 , \tag{2.1}$$

with the proportionality coefficient $\epsilon_{\rm an}$ characterizing the strength of the order induced by the nematic solvent (in Ref. [8] the scaled coefficient $\epsilon=\epsilon_{\rm an}/k_BT$ was employed). An explicit angular dependence is found for $U(\Omega)$, unless a spherical solute is considered, because the contribution $P_2(\mathbf{d}\cdot\mathbf{s})$ of a given surface element depends on the orientation Ω of the solute. The corresponding distribution

$$P(\Omega)=\exp\{-U(\Omega)/k_BT\}/\int d\Omega\exp\{-U(\Omega)/k_BT\} \tag{2.2}$$

allows the determination of the complete order matrix of the solute by performing the proper orientational averages. The only required information, besides parameter $\epsilon_{\rm an}$, is the profile of the solute surface, with the implicit assumption that specific interactions between nematic solvent and any functional group of the solute are absent, otherwise the pseudopotential would not scale with the area of surface elements. The application of this phenomenological model to a variety of solute molecules in calamitic nematic phases has demonstrated that the experimental order parameters are satisfactorily reproduced with the strength parameter $\epsilon_{\rm an}$ in the range 4 $\text{nm}^{-2}\le\epsilon_{\rm an}/k_BT\le 7\ \text{nm}^{-2}$ at about room temperature [8].

In order to give a physical interpretation to this phenomenological model, let us consider a macroscopic solute. Then the solute-solvent interactions can be described in terms of anchoring (Helmholtz) free energy A by using for instance the Rapini-Papoular equation [9,10]

$$A(\theta)\propto\sin^2(\theta-\theta_s) , \tag{2.3}$$

where θ is the tilt angle formed by the director $\mathbf{d}$ with respect to the planar surface, and θ_s is the preferred orientation. In the presence of unstructured surfaces which interact with the nematic solvent because of excluded volume effects, it should be natural to choose $\theta_s=0$ (planar degenerate anchoring) in the case of calamitic nematics, and $\theta_s=\pi/2$ (homeotropic anchoring) in the case of discotic liquid crystals. Then the anchoring free energy for a planar surface of area S can be written as

$$A(\theta)=\epsilon_{\rm an}S(3\sin^2\theta-1)/2 , \tag{2.4}$$

where the Rapini-Papoular Eq. (2.3) has been modified by including a constant additive term. Notice that the free energy has been scaled according to the surface area S. The absolute value of $\epsilon_{\rm an}$ determines the anchoring strength of the nematic solvent, defined as the change of the free energy for a unitary planar surface by operating a 90° shift of the tilt angle. On the other hand, the sign of $\epsilon_{\rm an}$ differentiates the calamitic nematics (positive $\epsilon_{\rm an}$) from discotic nematics (negative $\epsilon_{\rm an}$). The overall free energy of a solute of given shape is derived by integrating on the surface the infinitesimal contributions calculated according to Eq. (2.4). By noting that $\sin\theta=\pm\mathbf{d}\cdot\mathbf{s}$, Eq. (2.1) is recovered so supplying an interpretation of the phenomenological model in terms of surface anchoring. Moreover this implies that pseudopotential $U(\Omega)$ of Eq. (2.1) should be more correctly understood as the Helmholtz free energy for solute-solvent interactions. On the other hand, Eq. (2.2) represents the distribution on the fluctuations of solute orientations in the presence of a uniformly aligned director $\mathbf{d}$ (and fixed temperature and volume of the solution), and one can identify $U(\Omega)=A(\Omega)$ with the free energy change required by these fluctuations [11]. It might appear surprising that such a treatment for macroscopic objects can be applied also to a molecular solute. However, analogous macroscopic models of the solute, with the solvent treated as a continuum, have often been employed to derive molecular parameters, as in the Stokes-Einstein theory of diffusion coefficients or the calculation of solvation free energies [12].

Relation (2.1) interpreted as anchoring free energy of a generic solute in the presence of a nematic solvent, is the fundamental ingredient of our model of an induced cholesteric phase. Let us consider a sample of volume V at temperature T containing $N_{\rm nem}$ molecules of nematic solvent and N molecules of a chiral solute. The overall free energy A is decomposed into a term $A_{\rm nem}$ due to bulk interactions of the solvent and the contribution $A_{\rm ch}$ of surface interactions between the molecules of chiral solute and the solvent. A continuum representation is used for the solvent by considering explicitly only the twist elastic modes which could be stabilized by surface interactions with chiral solute. Afterwards the equilibrium pitch of the induced cholesteric phase will be derived as the free energy minimum with respect to the possible twist deformation. As often done in this type of stability analysis [13], we will employ for $A_{\rm nem}$ a single mode parametrization in correspondence of wave number q of a coherent twist deformation (the corresponding pitch being $p=2\pi/q$)

$$A_{\rm nem}=N_{\rm nem}\hat{K}_{2,2}q^2/2 , \tag{2.5}$$

where $N_{\rm nem}$ is the number of solvent molecules in the sample, and $\hat{K}_{2,2}$ is the twist force constant for molecule of the solvent (it is given by the relation $\hat{K}_{2,2}=K_{2,2}v_{\rm nem}/N_A$, where $K_{2,2}$ is the conventional force constant for unit volume, $v_{\rm nem}$ is the molar volume of the solvent, and N_A is the Avogadro number).

For $q\neq 0$, the director field $\mathbf{d}=\mathbf{d}(\mathbf{r})$ depends explicitly on the position $\mathbf{r}$ within the sample. It is convenient to use the following representation with the pitch axis along the y axis $\mathbf{u}_y^L$ of the laboratory frame $(\mathbf{u}_x^L,\mathbf{u}_y^L,\mathbf{u}_z^L)$:

$$\mathbf{d}(\mathbf{r})=\mathbf{u}_z^L\cos qy+\mathbf{u}_x^L\sin qy\ , \tag{2.6}$$

where $y=\mathbf{r}\cdot\mathbf{u}_y^L$.

Let us now consider the solute contributions to the free energy. After introducing a molecular frame $(\mathbf{u}_x^M,\mathbf{u}_y^M,\mathbf{u}_z^M)$ for the solute, the configuration of the ith solute molecule is specified by its position $\mathbf{R}^i$ and its orientation Ω^i with respect to the laboratory frame. Equation (2.1) will be used for the contribution of each solute molecule to the overall free energy. In the presence of a twist deformation, each contribution depends on the solute displacement $\mathbf{R}^i$, besides its orientation Ω^i, because of the position dependence of the director field $\mathbf{d}(\mathbf{r})$. Moreover, it depends also on the wave number q of the twist distortion, which determines the magnitude of the changes in direction of $\mathbf{d}$ at different surface locations. The contribution of the ith solute should then be specified as $U(q,\mathbf{R}^i,\Omega^i)$, and the overall free energy of the chiral solute is written as

$$A_{\mathrm{ch}}(q,\Xi)=\sum_{i=1}^{N}U(q,\mathbf{R}^i,\Omega^i)\ , \tag{2.7}$$

where $\Xi=(\mathbf{R}^1,\Omega^1,\mathbf{R}^2,\Omega^2,\ldots,\mathbf{R}^N,\Omega^N)$ denotes the ensemble of variables required to specify the configurations of the solute molecules. Notice that contributions for interactions amongst solute molecules are neglected. Therefore this relation can be applied only to dilute enough solutions of the chiral compound, so that an ideal behavior can be assumed.

In conclusion, one can write the following equation for the overall free energy:

$$A(q,\Xi)=A_{\mathrm{nem}}(q)+A_{\mathrm{ch}}(q,\Xi)\ , \tag{2.8}$$

which allows the calculation of the distribution function for fluctuations on (q,Ξ) variables:

$$P(q,\Xi)=\exp\{-A(q,\Xi)/k_BT\}\Big/\int dq\,d\Xi\exp\{-A(q,\Xi)/k_BT\}\ . \tag{2.9}$$

These fluctuations can be differentiated on the basis of their time scale. Fast processes like rotational and translational diffusion of single solute molecules determine the relaxation of Ξ variables, while much longer times are expected for large scale rearrangements required to modify q. In a coarse grained picture the distribution of twist deformation fluctuations becomes meaningful, and it can be derived by integrating Eq. (2.9) on the solute degrees of freedom

$$P(q)\equiv\int d\Xi\,P(q,\Xi)=\frac{I(q)^N\exp\{-A_{\mathrm{nem}}(q)/k_BT\}}{\int dq\,I(q)^N\exp\{-A_{\mathrm{nem}}(q)/k_BT\}}\ , \tag{2.10}$$

where the q-dependent integral

$$I(q)\equiv(1/V)\int d\Omega\,d\mathbf{R}\exp\{-U(q,\mathbf{R},\Omega)/k_BT\} \tag{2.11}$$

derives from the independent contributions of each solute molecule, V being the volume of the sample. The reduced distribution can be recast as

$$P(q)=\exp\{-A_d(q)/k_BT\}\Big/\int dq\exp\{-A_d(q)/k_BT\}\ , \tag{2.12}$$

with the following definition for the free energy $A_d(q)$ of twist deformation of the overall sample

$$A_d(q)=A_{\mathrm{nem}}(q)-Nk_BT\ln I(q)\ , \tag{2.13}$$

with the second term at the right hand side taking into account the contribution of the chiral solute. This is an effective free energy for fluctuations of twist deformation, since the dependence on the solute degrees of freedom has been averaged out. The equilibrium state of the system can be obtained from the minimum of $A_d(q)$, that is, the most probable system configuration with respect to the fluctuations. A finite pitch is recovered for chiral solute molecules since for them $I(-q)\neq I(q)$, so breaking the even symmetry of the solvent component $A_{\mathrm{nem}}(q)$.

As a self-consistency test of our treatment, one can show that cholesteric phases cannot be induced by achiral solute. Let us consider, for example, a solute which is symmetric with respect to a given mirror plane, and the change of $U(q,\mathbf{R},\Omega)$ after the application of such a symmetry operation. The elementary surface contributions $P_2(\mathbf{d}\cdot\mathbf{s})$ in Eq. (2.1) do not change by considering the mirror image of the solute and of the surrounding solvent, while the pitch of director field changes the sign. However, one should take into account that the direction of the pitch is modified by such a reflection, so that a new set $(\mathbf{R}',\Omega')$ of coordinates have to be assigned to the solute if the representation Eq. (2.6) of the director field must be preserved. This implies that a correspondence exists between coordinates $(\mathbf{R},\Omega)$ and $(\mathbf{R}',\Omega')$ such that $U(q,\mathbf{R},\Omega)=U(-q,\mathbf{R}',\Omega')$. In the integration on the solute degrees of freedom in Eq. (2.11), one can change the variables from $(\mathbf{R},\Omega)$ to $(\mathbf{R}',\Omega')$, so that $I(q)=I(-q)$. The distortion free energy $A_d(q)$ is then a symmetric function with the minimum at $q=0$ which corresponds to an ordinary nematic phase. The same kind of considerations can be applied to a solute possessing an inversion center or any improper axis of rotation. In the same way one justifies the change of sign of the pitch when a chiral solution is substituted by its mirror image, since in this case $I(q)$ should be replaced by $I(-q)$.

To conclude this section we emphasize that $I(q)$ is independent of the choice of the molecular frame. In fact, according to definition Eq. (2.11), $I(q)$ is obtained by averaging over all solute configurations the Boltzmann factor for the pseudopotential U which, according to Eq. (2.1), is determined only by the relative orientation between surface elements and the local director field $\mathbf{d}(\mathbf{r})$. Thus, a change of the molecular frame for a given configuration of the solute with respect to the director field, would not change the integrand of Eq. (2.11). The choice of a molecular frame is required only in the sampling of solute configurations according to variables $\mathbf{R}$ and Ω. In this framework we notice that the integration of solute position $\mathbf{R}$ in Eq. (2.11) can be avoided. In fact, for a given position $\mathbf{R}$, all the orientations of the solute with respect to the local director field are sampled by integrating on Ω. Therefore an identical contribution would result by changing the solute position, and Eq. (2.11) can be simplified as

$$I(q)=\int d\Omega \exp\{-U(q,0,\Omega)/k_B T\} \ , \tag{2.14}$$

having chosen for convenience $\mathbf{R}=0$ as the arbitrary value for the solute position.

III. TWISTING POWER OF A SOLUTE

All the ingredients of the model have been specified in Sec. II, and now the equilibrium state of the system has to be derived by considering the wave number q_{eq} of the twist deformation which minimizes the distortion free energy:

$$A_d'(q_{\text{eq}})=0 \ , \tag{3.1}$$

where the prime denotes the derivatives of q functions. From the previous result Eq. (2.13), the following equation is derived:

$$\frac{1}{pc}=\frac{k_B T}{2\pi \hat{K}_{2,2}}\frac{I'(q_{\text{eq}})}{I(q_{\text{eq}})} \ , \tag{3.2}$$

where $p=2\pi/q_{\text{eq}}$ is the equilibrium pitch, $c\equiv N/N_{\text{nem}}$ is the solute concentration as a ratio of molecule numbers with respect to the solvent. Let us consider the limit of Eq. (3.2) for $q_{\text{eq}}\rightarrow 0$, in correspondence of decreasing concentrations of the solute. The right hand side becomes a constant

$$\beta=\frac{k_B T}{2\pi \hat{K}_{2,2}}\frac{I'(0)}{I(0)} \ , \tag{3.3}$$

and in this limit the inverse proportionality between cholesteric pitch and concentration is recovered from the left hand side of Eq. (3.2)

$$1/p=\beta c \ . \tag{3.4}$$

Correspondingly, Eq. (3.3) provides a microscopic relation for the twisting power β in terms of the solute shape.

In order to specify in detail the relation between twisting power β and solute shape, we introduce the orienting potential $U_0(\Omega)$ acting on the solute in the nematic phase ($q=0$). According to Eq. (2.1) it can be written as

$$U_0(\Omega)\equiv U(0,\mathbf{R},\Omega)=\epsilon_{\text{an}}\int_S dS[3(\mathbf{s}\cdot\mathbf{u}_z^L)^2-1]/2 \ , \tag{3.5}$$

since, from Eq. (2.6), $\mathbf{d}=\mathbf{u}_z^L$ for $q=0$. The orientational dependence can be isolated from the surface integral by expressing the components of $\mathbf{s}$ in the molecular frame

$$U_0(\Omega)=-\sqrt{3/2}\,\epsilon_{\text{an}}\sum_{k,k'} E_{z,k}(\Omega)E_{z,k'}(\Omega)T_{k,k'} \ , \tag{3.6}$$

where the Euler matrix connecting the axes of the laboratory and molecular frames is denoted as

$$E_{j,k}(\Omega)\equiv \mathbf{u}_j^L\cdot\mathbf{u}_k^M \ . \tag{3.7}$$

The traceless matrix T defined in the molecular frame as

$$T_{k,k'}\equiv\sqrt{3/8}\int_S dS[\delta_{k,k'}-3(\mathbf{s}\cdot\mathbf{u}_k^M)(\mathbf{s}\cdot\mathbf{u}_{k'}^M)] \ , \tag{3.8}$$

correlates the orienting potential felt by the solute in the nematic phase with the anisotropy of its shape [8]. By using Wigner matrices to express the orientational dependence, potential $U_0(\Omega)$ can be written as

$$U_0(\Omega)=-\epsilon_{\text{an}}\sum_m D^2_{0,m}(\Omega)T^{(2,m)*} \ , \tag{3.9}$$

where $T^{(2,m)}$ are the second rank spherical components of Cartesian tensor $\mathbf{T}$. This allows the calculation of the orientational distribution of the solute in the nematic phase

$$P_0(\Omega) =\exp\{-U_0(\Omega)/k_B T\}\Big/\int d\Omega \exp\{-U_0(\Omega)/k_B T\} \ , \tag{3.10}$$

and the corresponding averages of functions $f(\Omega)$ will be denoted in the following as

$$\overline{f(\Omega)}\equiv\int d\Omega f(\Omega)P_0(\Omega) \ . \tag{3.11}$$

We mention that distribution Eq. (3.10) can be used for the calculation of solute orientational averages also in the induced cholesteric. As long as the pitch is much larger than molecular dimensions of the solute so that changes of the director field in different positions of solute surface are very small, then $U_0(\Omega)$ of Eq. (3.9) well approximates the mean-field potential acting on the solute. Of course, in this case, one should take into account that the cholesteric phase is characterized by a distribution of the director in the plane orthogonal to the helical axis, and a corresponding average has to be applied to the result of Eq. (3.11) in order to reproduce the experimental order parameters measured for instance in nuclear magnetic resonance (NMR) experiments. Then one can determine parameter ϵ_{an} for the chiral solute by generalizing the procedure of Ref. [8] for nematic phases.

By inserting Eq. (2.14) into Eq. (3.3) for the twisting power, one obtains

$$\beta=-\overline{U_1(\Omega)}/2\pi\hat{K}_{2,2} \ , \tag{3.12}$$

where $U_1(\Omega)$ describes the deviations of the solute pseudopotential in the induced cholesteric phase with respect to that of the nematic phase ($q=0$)

$$U_1(\Omega)\equiv[\partial U(q,0,\Omega)/\partial q]_{q=0} \ . \tag{3.13}$$

By taking into account that the q dependence of pseudopotential Eq. (2.1) derives from the position dependence of the director field Eq. (2.6), the following explicit form is derived:

$$U_1(\Omega)=3\epsilon_{\rm an}\int_S dS(\mathbf{s}\cdot\mathbf{u}_x^L)(\mathbf{r}\cdot\mathbf{u}_y^L)(\mathbf{s}\cdot\mathbf{u}_z^L) \ , \tag{3.14}$$

where $\mathbf{r}$ is the position vector in the laboratory frame of a given surface element (it should be recalled that by choosing $\mathbf{R}=0$ in Eq. (2.14), the origins of molecular and laboratory frames coincide). As for the nematic potential Eq. (3.5), one can specify the orientational dependence by expressing vector components of $\mathbf{s}$ and $\mathbf{r}$ in the molecular frame:

$$U_1(\Omega)=-\epsilon_{\rm an}\sum_{k,k',k''} E_{x,k}(\Omega)E_{y,k'}(\Omega)E_{z,k''}(\Omega) \times Q_{k,k',k''} \ , \tag{3.15}$$

with the matrix Q defined in the molecular frame by integration on the solute surface

$$Q_{k,k',k''}=-3\int_S dS(\mathbf{s}\cdot\mathbf{u}_k^M)(\mathbf{r}\cdot\mathbf{u}_{k'}^M)(\mathbf{s}\cdot\mathbf{u}_{\rm k''}^{\rm M}) \ . \tag{3.16}$$

The final result for the twisting power is

$$\beta=\epsilon_{\rm an}\mathcal{Q}/2\pi\hat{K}_{2,2} \ , \tag{3.17}$$

where we have introduced the chirality order parameter

$$\mathcal{Q}\equiv\sum_{k,k',k''}\overline{E_{x,k}(\Omega)E_{y,k'}(\Omega)E_{z,k''}(\Omega)Q_{k,k',k''}} \ . \tag{3.18}$$

The definition of $\mathbf{Q}$ of Ref. [7] has been modified by inserting a factor (-1) in order to deal with parameters β and $\mathcal{Q}$ having the same sign for positive $\epsilon_{\rm an}$. By using the spherical tensor notation, Eq. (3.18) is transformed into the following convenient form:

$$\mathcal{Q}=(i/2)\sum_m\overline{D^2_{0,m}(\Omega)}Q^{(2,m)*} \ , \tag{3.19}$$

where $\overline{D^2_{0,m}(\Omega)}$ are the orientational order parameters for the solute in the nematic field, and the second-rank components $Q^{(2,m)}$ of $\mathbf{Q}$ are given explicitly in Table I. Notice that $\mathcal{Q}$ depends not only on the solute shape through $\mathbf{Q}$ of Eq. (3.16), but also on the temperature and the anchoring strength parameter $\epsilon_{\rm an}$ because of the presence of the orientational order parameters. In Ref. [14] a detailed analysis of the independent elements of $Q^{(2,m)}$ and of the orientational order dependence of the chirality order parameter is presented for different molecular systems.

TABLE I. The second-rank components of the $\mathbf{Q}$ matrix are listed.

$$Q^{(2,0)}=i(Q_{x,y,z}-Q_{y,x,z}) \ ,$$

$$\begin{aligned}Q^{(2,1)}&=Q^{(2,-1)*}\\&=(Q_{x,y,y}-Q_{y,x,y}+Q_{z,x,z}-Q_{x,z,z})/\sqrt{6}\\&\quad+i(Q_{x,x,y}-Q_{x,y,x}+Q_{z,y,z}-Q_{y,z,z})/\sqrt{6},\end{aligned}$$

$$\begin{aligned}Q^{(2,2)}&=-Q^{(2,-2)*}\\&=(Q_{x,z,x}-Q_{x,x,z}+Q_{y,y,z}-Q_{y,z,y})/\sqrt{6}\\&\quad-i(Q_{x,y,z}-2Q_{x,z,y}+Q_{y,x,z})/\sqrt{6}.\end{aligned}$$

The chirality order parameter can be used to characterize the asymmetry of the solute shape, since the cholesteric pitch would be inversely proportional to $\mathcal{Q}$ when considering different solute at the same concentration in the same solvent [and temperature since $\hat{K}_{2,2}=\hat{K}_{2,2}(T)$]. We mention that the chirality order parameter is independent of the choice of the molecular frame for the solute, in spite of the reference to such a frame in definition (3.16) of matrix $\mathbf{Q}$. In fact the twisting power has been derived from the minimization of the distortion free energy $A_d(q)$ Eq. (2.13) which, as emphasized at the end of Sec. II, is invariant with respect to the choice of the molecular frame and of its origin in particular. Therefore the minimum $q_{\rm eq}$ as well as all the related parameters β and $\mathcal{Q}$, are independent of this choice. The use of a particular molecular frame is dictated only by need of computing the surface integrals.

The chirality order parameter, and therefore also the twisting power β once the twist elastic constant $\hat{K}_{2,2}$ has been determined for the nematic solvent, can be easily calculated from the solute shape by means of a simple surface integration. Only the anchoring strength $\epsilon_{\rm an}$ needs to be specified but, as found in Ref. [8], usually it is confined in a limited range (cf. Sec. II). Moreover one can determine it from the measure of orientational order parameters of the solute, as mentioned previously. Therefore the accuracy of our phenomenological model in predicting the twisting power can be self-consistently established by means of simultaneous measurements of orientational order parameters of the solute and of the pitch of the induced cholesteric phase.

To conclude this section, some simple generalizations of the previous treatment will be presented. First we consider the cholesteric phase induced by the simultaneous presence of M different types of solute. As long as the interactions amongst the solute molecules can be neglected, the solute free energy is calculated by including the contribution $A^{(m)}_{\rm ch}$ of each species

$$A_{\rm ch}=\sum_{m=1}^{M}A^{(m)}_{\rm ch} \ . \tag{3.20}$$

Then $I(q)^N$ in Eq. (2.10) for the distribution $P(q)$ should be replaced by

$$\prod_{m=1}^{M}I^{(m)}(q)^{N_m} \ , \tag{3.21}$$

where $I^{(m)}(q)$ is the integral Eq. (2.11) for the mth species and N_m the corresponding number of molecules in the sample. By writing the free energy of twist distortions as

$$A_d(q)=A_{\rm nem}(q)-k_BT\sum_{m=1}^{M}N_m\ln I^{(m)}(q) \ , \tag{3.22}$$

one can easily generalize the previous analysis of this section, so recovering a linear relationship between the inverse pitch and the contribution of each species

$$1/p = \sum_{m=1}^{M} c_m \beta_m \ , \tag{3.23}$$

where $c_m \equiv N_m / N_{\text{nem}}$ is the concentration of the mth solute with a twisting power β_m calculated according to Eq. (3.17). An obvious consequence is the absence of the cholesteric phase for a racemic mixture of solute, i.e., two enantiomeric species ($\beta_1 = -\beta_2$) at the same concentration $c_1 = c_2$.

Up to now we have implicitly considered rigid solute. Also this constraint can be easily removed by taking into account the dependence of the solute surface and, therefore, also of the anchoring energy Eq. (2.1), on a suitable set $\mathbf{X}$ of internal coordinates describing the configurations of a flexible molecule. The effective potential acting on a given solute should then be modified as

$$U(q,\mathbf{R},\Omega,\mathbf{X}) = U_{\text{an}}(q,\mathbf{R},\Omega,\mathbf{X}) + U_{\text{int}}(\mathbf{X}) \ , \tag{3.24}$$

where U_{an} is the surface anchoring energy defined by Eq. (2.1), and U_{int} the intramolecular potential, i.e., the mean-field potential for the internal degrees of freedom when the molecule is in the isotropic phase. Now the state variables Ξ for the solute should include also the internal coordinates $\mathbf{X}^1, \mathbf{X}^2, \ldots, \mathbf{X}^N$, and $I(q)$ function in the distortion free energy $A_d(q)$ of Eq. (2.13) is generalized to the following form:

$$I(q) = (1/V) \int d\Omega \, d\mathbf{R} \, d\mathbf{X} \exp\{-U(q,\mathbf{R},\Omega,\mathbf{X})/k_B T\} \ . \tag{3.25}$$

The treatment of this section can also be applied to this case, once one takes into account the dependence of the surface integrals Eq. (3.5) and Eq. (3.16) on the internal coordinates $\mathbf{X}$ whose distribution in the nematic phase is given as

$$P(\mathbf{X}) = \frac{\int d\Omega \exp\{-U(0,\mathbf{R},\Omega,\mathbf{X})/k_B T\}}{\int d\Omega \, d\mathbf{X} \exp\{-U(0,\mathbf{R},\Omega,\mathbf{X})/k_B T\}} \ . \tag{3.26}$$

By considering the solute in a particular configuration $\mathbf{X}$, Eq. (3.18) or Eq. (3.19) can be used to derive the $\mathbf{X}$-dependent chirality order parameter $\mathcal{Q}(\mathbf{X})$ by inserting the orientational order parameters $D^2_{0,m}(\Omega)$ specific for such a configuration. Then the average on the internal coordinates is required in order to calculate its mean value

$$\mathcal{Q} = \int d\mathbf{X} \, \mathcal{Q}(\mathbf{X}) P(\mathbf{X}) \ , \tag{3.27}$$

to be inserted in relation (3.17) for the effective twisting power β.

IV. AN EXAMPLE: THE BINAPHTHYL MOLECULE

In order to illustrate an application of the proposed method, we consider the 1,1′-binaphthyl molecule which is drawn in Fig. 1. The calculations have been done for different values of the torsional angle θ between the two naphthyl rings (see Fig. 1). As in Ref. [8], the solute surface was derived from superposition of van der Waals spheres [15] with standard values for bond lengths and bond angles [16]. By using an anchoring strength $\epsilon_{\text{an}}/k_B T = 5 \text{ nm}^{-2}$ at $T = 300$ K, which should be appropriate for nematic liquid crystals in their intermediate range of the orientational order parameter, we obtain the chirality order parameter $\mathcal{Q}(\theta)$ shown in Fig. 2 as a function of the torsional angle. Only the data for the range $0° \le \theta \le 180°$ are reported because of the symmetry relation $\mathcal{Q}(-\theta) = -\mathcal{Q}(\theta)$. In fact the change of sign of θ is recovered by performing a reflection through a molecular plane, so changing also the sign of the chirality order parameter.

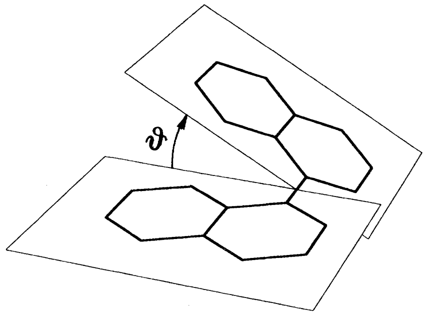

FIG. 1. The binaphthyl molecule. The direction of the torsional angle θ towards positive values is shown in the figure.

Notice that for $0° \le \theta \le 180°$, the chirality order parameter is positive for the cisoid configuration ($\theta \sim 45°$), and negative in the transoid configuration ($\theta \sim 135°$). Since $\mathcal{Q}(\theta)$ is a continuous function of θ, it must vanish at an intermediate value of the torsional angle ($\theta \simeq 93°$), without requiring a particular symmetry of the molecular system. On the contrary, the vanishing of $\mathcal{Q}$ at $\theta = 0°$ and

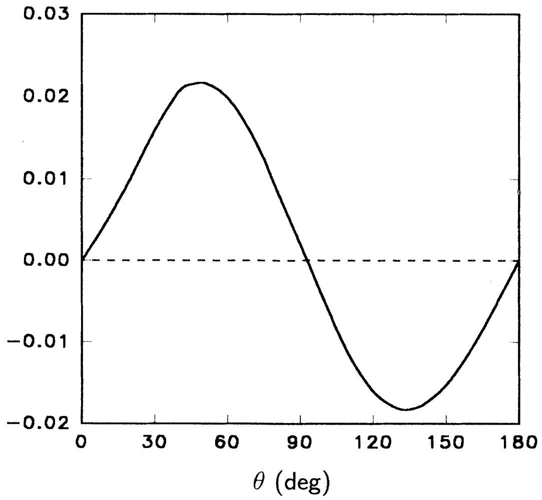

FIG. 2. Chirality order parameter $\mathcal{Q}$ as function of the torsional angle θ for the binaphthyl molecule. An anchoring strength $\epsilon_{\text{an}}/k_B T = 5 \text{ nm}^{-2}$ at $T = 300$ K was employed.

$\theta = 180°$ is due to the presence of a symmetry plane in the molecule in these configurations.

In ordinary solutions of binaphthyl, all the torsional angle configurations are allowed with an even distribution on the torsional angle θ. Therefore, the average Eq. (3.27) of the chirality order parameter over the torsional angle ($\mathbf{X} = \theta$ in this case) vanishes together with the twisting power β. In order to observe an induced cholesteric phase, the torsional angle should be constrained. This has been done by linking the 2 and 2′ positions of the naphthyl rings with an ethylenic or a disulfide bridge [2,17]. For the binaphthyl with the ethylenic bridge, Gottarelli and Spada have measured a twisting power $\beta = 37\ \mu\mathrm{m}^{-1}$ in *N*-(4′-methoxybenzylidene-4-(*n*-butyl)aniline (MBBA) when the twist force constant of the pure liquid crystal is $K_{2,2} = 3.2 \times 10^{-12}$ N ($\hat{K}_{2,2} = 1.6 \times 10^{-35}$ N m^3 by estimating the molar volume of MBBA as $v_{\mathrm{nem}} \simeq 0.30 \times 10^{-3}$ m^3). Given the rough similarity between ethylenic and disulfide bridges, one can use the value $\theta = 56°$ measured in the latter compound [18]. From Fig. 2 we estimate the order parameter as $\mathcal{Q} \simeq 0.021$ nm^3, and from Eq. (3.16) the twisting power $\beta \simeq 43\ \mu\mathrm{m}^{-1}$ which is in agreement with the experimental result. A more precise comparison with our theoretical model would require detailed information about the molecular geometry (i.e., the torsional angle, but given the maximum of $\mathcal{Q}(\theta)$ near $\theta \simeq 50°$, it should not deeply modify the previous result), and the anchoring strength ϵ_{an} through determinations of the orientational order parameters of the solute.

It should be mentioned that the twisting power has been measured also in the derivative of the binaphthyl with methyl groups in positions 2 and 2′, which prevent the racemization by constraining the torsional angle in the range $0° \leq \theta \leq 180°$ [2]. In this case one measures a much smaller value of the twisting power $\beta \simeq 0.5\ \mu\mathrm{m}^{-1}$ when compared to the constrained binaphthyl. An obvious explanation is supplied by the profile of $\mathcal{Q}(\theta)$ shown in Fig. 2, because of the change of sign by going from cisoid to transoid configurations. Detailed calculations according to Eq. (3.27) would require a model for the distribution on the torsional angle. However, if we suppose that, in analogy to the biphenyl molecule [19], the intramolecular potential confines the angle θ to narrow ranges around $\theta \sim 45°$ and $\theta \sim 135°$ in correspondence of two conformations with about the same population, small values of the averaged chirality order parameter and of the twisting power would be obtained like in the experimental result.

V. CONCLUSIONS

By means of a continuum representation of the twist deformation of the nematic solvent and by approximating its interactions with a solute like the anchoring energy of a macroscopic surface, a simple model for the induced cholesteric phase has been derived. The straightforward application of statistical methods allows the determination of the twisting power of a chiral solute in terms of an order parameter related to the asymmetry of the solute shape. As applications, the binaphthyl molecule and parent compounds have been considered with a substantial agreement with the experimental results. A more accurate comparison of theoretical predictions with measured twisting powers would require an independent determination of the anchoring strength ϵ_{an} for a specific system by means of the orientational order parameters of the solute [8].

Given the simplifying assumptions invoked to describe the nematic solvent and the solute-solvent interactions, our theory has necessarily a phenomenological character, the understanding of the influence of the solute shape on the stabilization of the cholesteric twist deformation being its main purpose. Of course the real phenomena might be more complicated because of specific interactions between solute and solvent, which cannot be assimilated to the simple model of the anchoring energy of a surface. Certainly these specific interactions could play a major role in the presence of a weak stabilization due to the solute shape, i.e., when the chirality order parameter $\mathcal{Q}$ of Eq. (3.18) is small in correspondence of a solute with low twisting power. On the other hand the effects of these specific interactions can be minimized by a judicious choice of the molecular system.

Finally we would like to mention how our results can be employed to quantify the molecular chirality. Much work has been recently dedicated to the derivation of a suitable parameter characterizing the chirality in the spatial organization of a molecule. In particular, measures of chirality have been introduced on the basis of geometric concepts only [20,21]. As alternative one can use a physical phenomenon produced by the molecular chirality as a reference for its measure, as done by Osipov, Pickup, and Dunmur on the basis of the optical activity [22]. In this framework one can consider also the pitch of induced cholesterics. Then a convenient measure of the molecular chirality could be the order parameter $\mathcal{Q}$ of Eq. (3.18). However, one should take into account that $\mathcal{Q}$ depends not only on the molecular shape, but also on the temperature and the anchoring strength ϵ_{an} through the solute orientational order parameters. In order to standardize such a chirality measure, one might fix a reasonable value for the ratio $\epsilon_{\mathrm{an}}/k_B T$, or consider the scaled parameter $\mathcal{Q}' = \mathcal{Q} k_B T / \epsilon_{\mathrm{an}}$ for hypothetical solvents with a low anchoring strength. In fact $\mathcal{Q}'$ depends only on the molecular shape in the limit $\epsilon_{\mathrm{an}} \rightarrow 0$, and it is easily calculated by representing the molecule as an ensemble of van der Waals spheres.

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