Helicoidal Cholesteric Phase

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***Abstract* - We present a mean field theory for higher order legendre polynomial in chiral interaction part to describe helicoidal cholesteric phase for binary mixture of chiral nematic liquid crystals and polymer chain in presence of longitudinal electric field which is parallel to the pitch axis of cholesteric phase. We have calculated free energy of the helicoidal cholesteric phase a a function of order parameter and orientational distribution function in equilibrium state. Based on free energy minimization we have observed that inclusion of higher order legendre polynomial in intermolecular potential makes ChH phase more stabilized depending on the external field strength.**

***Index Terms* - Legendre Polynomial, Cholesteric Phase, Helicoidal Cholesteric phase, Distortion free energy, Order parameter and External field.**

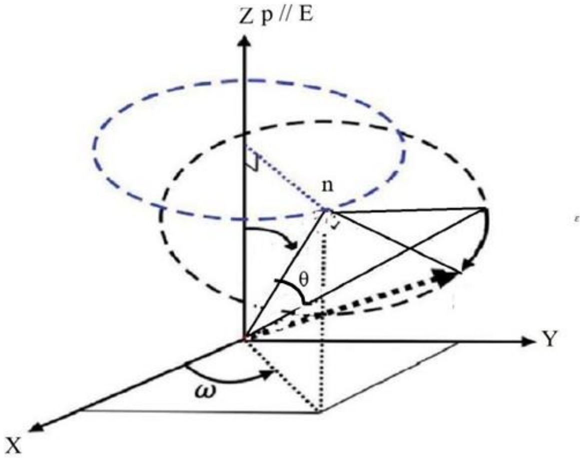

Figure 1. Illustration of the director with the cone angle between the director and the pitch axis under the external electric field

INTRODUCTION

Liquid Crystal has an important role in application and the influenced of external field i.e electric or magnetic field on Cholesteric or chiral nematic N* phase are the one of the important for many technological applications, biological materials, fundamental physical and chemical research. When an electric or magnetic field is applied perpendicular towards helical axis of a cholesteric phase, untwisting of helix takes place with positive diamagnetic anisotropy or positive dielectric above the threshold value of the electric or magnetic field. This is well known as field- induced twist-untwist transitions [1-10]. When the longitudinal electric or magnetic field is applied parallel towards helical axis of cholesteric phase, the director **n** exhibits a helicoidal structure, this was first theoretically observed by Meyer [11] and experimentally investigated [12]. The director of helicoidal cholesteric liquid phase has the same as twist- bend nematic phase in achiral bent- core liquid crystals molecules [13-25]. In recent times researcher have shown interest in both cholesteric and twist- bend nematic phase.

Recently, many mean field theories presented to describe the cholesteric liquid crystal molecules in presence of the external electric field perpendicular towards pitch axis and also in mixture of cholesteric phase of a polymer chain [26-32]. In all these theories we have seen that the intermolecular interactions have been truncated by lower order of legendre polynomial i.e. intermolecular chiral interaction is given by $(\Omega_1 \times \Omega_2 \cdot r_{12})\ P_1\ (\Omega_1 \cdot \Omega_2)$ in the lowest order. The chiral interaction must be odd in $\boldsymbol{\Omega_1 \cdot \Omega_2}$ while in nematic interaction be even. The existence of this term differentiates cholesterics from nematics and determines the cholesteric pitch in an equilibrium state. Theoretically all these models based on general molecular model of choleteric liquid crystals presented by Liu- Liu group. They proposed a planar model containing the intermolecular potential is contain chiral contributions and by mean field theory they observed the microscopic basis of the existence of cholesteric phase [33]. In [34] a Molecular theory for cholesteric liquid crystals they observed that by symmetry considerations a general form of intermolecular potential contains chiral term which are the reason for forming cholesteric liquid crystal. Maier and Saupe [35] offered a generalized theory known as Maier Saupe theory and this theory is widely used for the understanding of mean field analysis for intermolecular potential used in all this kind of phase transitions problems.

In all the theoretical attempts to describe cholesteric phase, we have seen that the chiral potential in series of legendre polynomial truncated by lower order of legendre polynomial. We focus on the theoretical understanding of phase transitions properties of the cholesteric liquid crystals phase in presence of external electric field which is parallel to the pitch axis of the cholesteric phase by taking higher order legendre polynomial in chiral potential in intermolecular potential.

The coupling between director and the external field i.e. electric field, we developed our mean field theory for higher order legendre polynomial in chiral interaction potential. The aim of this work is to developed theoretical understanding of cholesteric liquid crystal phase in presence of external field for higher order legendre polynomial in interaction potential.

Based on model for higher order legendre polynomial in chiral interactions, we derive the free energy of the helicoidal cholesteric phase as a function of orientational order parameter of a Liquid crystal molecules and the order parameter of the liquid crystals. Using these order parameters, we theoretically predicted isotropic phase, paranematic phase, Usual nematic phase and cholesteric and helicoidal cholesteric phase.

FREE ENERGY OF A HELICOIDAL CHOLESTERIC PHASE

Let us consider a binary mixture of a Liquid Crystals and a flexible polymer chain. For the analysis of helicoidal cholesteric phase of binary mixture, we developed our theory based on molecular theory of Liu- Liu et al. [33-34] and other models for lower order of legendre polynomial [35-36].

Let Np be the number of polymers with np segments and N_L be the low- molecular weight liquid molecules of length L and Diameter D. The volume of LC molecule and of polymer chain is $V_L = \left(\frac{\pi}{4}\right) D^2 L$ and $v_P = a^3 n_P$ respectively. Let us consider the volume fraction of both liquid crystal molecule and polymer chain is $\emptyset_L = v_L \rho_L$ and $\emptyset_P = v_P \rho_P$ respectively, where ρ_i is the number density. Due to axial ratio $n_L = \frac{L}{D}$ of liquid crystal molecule and volume per molecule is consider as $v_L = a^3 n_L$, where $a^3 = \frac{\pi}{4} D^3$.

The free energy is considered as

$$F = F_{mix} + F_{ani} \qquad (1)$$

In above mentioned equation the first term descries isotropic mixing of binary mixture and it is given by well-known Flory- Huggins theory for polymer [38].

$$a^3 \beta \frac{F_{mix}}{V} = \frac{\emptyset_L}{n_L} ln \emptyset_L + \frac{\emptyset_P}{n_P} ln \emptyset_P + \chi \emptyset_L \emptyset_P \qquad (2)$$

In equation (2), χ is defined as Flory- Huggins interaction parameter between the liquid crystal molecule and polymer chain in an isotropixc phase and $\beta = \frac{1}{k_B T}$; where T is absolute temperature and k_B is Boltzmann constant

The second term in equation (1) stands for free energy of liquid crystal phases including nematic, cholesteric and helicoidal cholesteric liquid crystals. The configuration of the constituent LC molecules is characterized by position vector **r** and orientation unit vector Ω defined by polar angle between local director n(r) and solid angle dΩ, Where $d\Omega = \sin\theta d\theta d\emptyset$. Let the orientational distribution function of the liquid crystal molecule is defined as f_L (n(r)·Ω). The distribution function depends on only relative angle between local director and molecular orientation vector. The anisotropic part of the free energy in the second virial approximation is given by

$$\beta F_{ani} = \rho_L \int f_L(\mathrm{n}(\mathrm{r}_1) \cdot \Omega_1) \ln 4\pi f_L(\mathrm{n}(\mathrm{r}_1) \cdot \Omega_1) d\mathrm{r}_1 d\Omega_1$$
$$+\frac{1}{2} \rho_L^2 \int f_L(\mathrm{r}_1 \cdot \Omega_1) f_L((\mathrm{r}_2 \cdot \Omega_2) \beta \mathrm{U}_{LL}(\mathrm{r}_1, \Omega_1; \mathrm{r}_2, \Omega_2) d\mathrm{R} \quad (3)$$

where $\beta = \frac{1}{k_B T}$; and T is absolute temperature and k_B is Boltzmann constant and

$$dR \equiv dr_1 dr_2 d\Omega_1 d\Omega_2$$

The first term in equation (3) represents the change in entropy because of orientational ordering and U_{LL} is for orientation dependent intermolecular potential between LC molecule at a position r_1 with an orientation Ω_1 and that at a position r_2 with an orientation Ω_2. In this work we are neglecting the effect of anisotropic coupling between the polymer and the LC molecule because we are only concerned on flexible polymers. The Higher- order chiral contributions to the interaction potential for the Liquid crystal phases are given in the series configuration of legendre polynomial [27,34,39,40]:

$$U_{LL}\ (\mathrm{r}_1, \Omega_1; \mathrm{r}_2, \Omega_2) = U_{LL,1}(\mathrm{r}_{12})(\Omega_1 \times \Omega_2 \cdot \hat{r}_{12})\mathrm{P}_1(\Omega_1 \cdot \Omega_2) + U_{LL,2}(r_{12})P_2\ (\Omega_1 \cdot \Omega_2) + \qquad (4)$$

where $\mathrm{r}_{12} = \mathrm{r}_1 - \mathrm{r}_2$.

In eq (4) the first and third term ($U_{\mathrm{LL},1}$and $U_{\mathrm{LL},3}$) shows chiral interaction between LC molecules. The term $(\boldsymbol{\Omega 1} \times \boldsymbol{\Omega 2} \cdot \boldsymbol{r}\text{^}\mathbf{12})$ is a pseudoscalar and $\boldsymbol{r}\text{^}\mathbf{12} \equiv (\mathbf{r2} - \mathbf{r1})\ /\ |(\mathbf{r2} - \mathbf{r1})|$ is unit vector. From experiment it is observed that in achiral system the twist deformation studied and for achiral

banana shaped molecules exhibit a conformal chirality within each molecule: left handed and right handed helices [18,37]. The chiral interaction ULL,1and ULL,3contribute in achiral system. The $U_{\mathrm{LL},2}$term in potential shows intermolecular potential which is responsible for nematic phases and used in the Maier-Saupe [35] and Onsager models [36]. We have assumed that the interaction potential ULL is short range (d_0) and we have defined cL = $-\ \beta$ (ULL,1 + ULL,3) for chiral pseudoscalar material parameter and vL = $-\beta U$LL,2(> 0) for nematic interaction parameter. The positive/ negative value of the chiral pseudoscalar material parameter responsible for left/ right-handed helix. The nematic interaction parameter has been defined in Maier- Saupe theory for the nematic phase [1,35]

In order for calculation of spatial variation of the director we are using tensor order parameter [1]

$$Q_{\alpha\beta}(\mathbf{r}) = S_L\ (\tfrac{3}{2} n_\alpha(\mathbf{r}) n_\beta(\mathbf{r}) - ½\ \delta_{\alpha\beta}) \qquad (5)$$

Where n_α and $\delta_{\alpha\beta}$represents the α (= x, y, z) components of the director **n** and kronecker delta function respectively. The scalar orientational order parameter S_{L} for the LC molecules can be obtained from

$$S_L = \int P_2(n(\mathbf{r}).\Omega) f_L(n(\mathbf{r}).\Omega)\ \mathrm{d}\Omega \qquad (6)$$

And it is independent of the position **r** for the bulk LC phase.

Substituting eq (5) into eq (3) and (4), the anisotropic free energy can be expressed as [27-32] -

$$F_{\mathrm{ani}} = F_{\mathrm{nem}} + F_{\mathrm{d}} \qquad (7)$$

where the first term is for nematic free energy and second term is for distortion free energy.

The nematic free energy is defined as

$$F_{\mathrm{nem}}\ \equiv\ a^3\beta\ F_{\mathrm{nem}}/V$$

$$= \frac{\emptyset_L}{n_L} \int f_L(n(\mathbf{r}).\Omega) \ln 4\pi f_L(n(\mathbf{r}).\Omega)\ \mathrm{d}\Omega - 1/2\ v_L\ \emptyset_L^2 S_L^2 \qquad (8)$$

The second term of equation (7), the distortion free energy containing first and second spatial derivatives of the tensor order parameter [27,30] ;

$$\frac{a^3\beta F_d}{V} = \frac{1}{4} v_L \frac{2}{9} d_0^2 \partial_\gamma Q_{\alpha\beta}(\boldsymbol{r}) \partial_\gamma Q_{\alpha\beta}(\boldsymbol{r}) - \frac{2}{9} c_L d_0 \varepsilon_{\alpha\beta\gamma} Q_{\mu\beta}(\boldsymbol{r}) \partial_\alpha Q_{\mu\gamma}(\boldsymbol{r}) \qquad (9)$$

where $\partial_\gamma = \partial/\partial \mathrm{r}$ is first spatial derivative of the tensor order parameter and $\varepsilon_{\alpha\beta\gamma}$ is the Levi-Civita anti-symmetric tensor of the third rank.

For this work we consider longitudinal external electric field parallel to the pitch axis p. The electric field is given by-

$$\mathbf{E} = (0,\ 0,\ E) \qquad (11)$$

where E represents the strength of the electric field.

When the dielectric anisotropy is positive the liquid crystal molecules tends to orients towards electric field. The longitudinal deformations along Z axis can orient the director along the pitch axis p, the directors rotates out perpendicular plane onto the surface of cone angle .The director is defined as-

$$n\ (z) = (\sin\epsilon \cos w(z)\ , \sin\epsilon \sin w(z)\ , \cos\epsilon) \qquad (12)$$

The cone angle is constant and does not depend on the position z. The director is uniformly twisted along z axis with pitch and the azimuthal angle ω is given as function of position which is ω = qz.

The dimensionless nematic free energy ($f$nem) is given as-

$$F_{\mathrm{nem}}\ \equiv\ a^3\beta\ F_{\mathrm{nem}}/V$$

$$= \frac{\emptyset_L}{\mathrm{n}_L} \int f_L(\mathrm{n}(\mathbf{r}) \cdot \Omega) \ln 4\pi f_L(\mathrm{n}(\mathbf{r}) \cdot \Omega)\mathbf{d}\Omega\ -\ ½\ v_L \emptyset_L^2 S_L^2 - \emptyset_L S_L h_L^2 \qquad (13)$$

SUMMARY AND CONCLUSION

In this work we have presented a mean field theory to understand the helicoidal cholesteric phase induced by an external field for third order legendre polynomial in intermolecular potential. From this theory we observed that the stable $\mathrm{Ch_H}$ phase can appear for K_{22}> K_{33} with $\mathrm{S_L}$>0. We observed that the inclusion of third order legendre polynomial in intermolecular potential leads to more stabilized helicoidal cholesteric phase in comparison with the previous few models which is truncated intermolecular potential for the lower order of legendre polynomial. In this work, we have focused on mixures of a flexible polymer and a liquid crystal molecule only and neglected the anisotropic coupling between liquid crystal molecule and polymer or any other molecules. When the order parameter y = 1 we have Q= Q0 this shows that Ch phase and when y = 0 we have nematic phase. For k2 > k3, we have the stable helicoidal phase.

REFERENCES

[1] The Physics of Liquid Crystals, ed. P.G.de Gennes and J. Prost (Oxford University Press, New York, 1993)

[2] Chirality in Liquid Crystals, ed. H-S.kitzerow and C. Bahr (Springer, New York, 2001)

[3] Fundamental of Liquid Crystals, ed Shri Singh

[4] R B Meyer. Appl Phys Lett. 14, 208-209 (1969)

[5] R B Meyer in Les Houches summer school in Theoretical Physics ed. R. G Balian and G Weil , Gordon and Briach, New York 1976 pp 273- 373

[6] PG De Gennes. Solid State Commun. 6, 163-165 (1968)

[7] G Durand, L Leger, F Rondelez, et al. Phys Rev Lett. 22, 227-228 (1969)

[8] C Motloc, I Cuculescu, M Honciuc, Mol Cryst Liq Cryst. 45, 215-219 (1978)

[9] HA Van Sprang, JLM Van De Venne. J. Allp. Phys. 57, 175-179 (1985)

[10] R. B. Meyer. Appl. Phys. Lett. 12, 281 (1968)

[11] J Xiang, SV Shiyanovshkii, C Imrie, et al. Phys Rev Lett. 112, 217801 (2014)

[12] I. Dozov, Europhys.Lett. 56, 247-253 (2001)

[13] S. M. Shamid, S. Dhakal and J. V. Selinger, Phys. Rev. E87, 052503 (2013)

[14] S. M. Shamid, D. W.Allender and J. V. Selinger, Phys. Rev. Lett. 113, 237801 (2014)

[15] G. Barbero, L. R. Evangelista, M. P. Rosseto, R. S. Zola and I. Lelidis, Phys. Rev. E. 92,

[16] V. Borshch, Y. K. Kim, J. Xiang, M. Gao, A. Jakli, V. P. Panov, J. K. Vij, C. T. Imrie, M.

[17] G. Tamba, G. H. Mehl and O. D. Lavrentovich, Nat. Commun. 4, 2635 (2013) 030501 (R) (2015)

[18] P.A. Henderson and C T Imrie, Liq. Cryst. 38,1407 (2011)

[19] C. Greco, G. R. Luckhurst and A. Ferrarini, Phys. Chem. Chem. Phys. 15, 14961 (2013)

[20] C. Meyer, G. R. Luckhurst and I.Dozov, Phys. Rev. Lett. 111, 067801 (2013)

[21] M. Cestari, S. Diez- Berart, D.A.Dunmur, A. Ferrarini, M.R. de la Fuente, D. J. B. Jackson, D. O. Lopez, G. R. Luckhurst, M. A. Perez- Jubindo, R. M. Richardson, J. Salud, B. A. Timimi and H. Zimmermann, Phys. Rev. E 84, 031704 (2011)

[22] D A Paterson, M Gao, Y K Kim, A Jamali, K L Finley, B R- Hernandez, S D- Berart, JSalud, M R de la Fuente, B A Timimi, H Zimmermann, C Greco, A Ferrarini, J M D Storey, D O Lopez, O D Lavrentovich, G R Luckhurst and C T Imrie Soft Matter, 201612, 6827

[23] J Pang, NA Clark. Phys. Rev. Lett. 73, 2332-2335 (1994)

[24] RRR De Almeida, C Zhang, O Parri et. Al. Liq. Cryst. 41, 1661-1667 (2014)

[25] C J Yun, MR Vengatesan, JK Vij Appl. Phys. Lett. 106, 173102 (2015)

[26] A. Matsuyama, J. Phys. Soc. Jpn 85, 114606 (2016)

[27] A. Matsuyama, J. Chem. Phys. 139, 174906 (2013)

[28] A. Matsuyama, J. Chem. Phys. 141, 184903 (2014)

[29] A. Matsuyama, Liq. Cryst. 42, 423 (2015)

[30] A. Matsuyama, Mol. Cryst. Liq. Cryst. 612,33 (2015)

[31] A. Matsuyama, Liq. Cryst. 43, 783-795 (2016)

[32] A. Matsuyama, Liq. Cryst. 45, 153-164 (2018)

[33] Y. R. Liu-Liu, Y.M. Shih, C. W. Woo, Phys. Rev. A 15,2550 (1977)

[34] Y. R. Liu-Liu, Y.M. Shih, C. W. Woo and H.T. Tan, Phys. Rev. A 14,445 (1976)