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Liquid crystals : refractive indices of monomers and discrete model of polar polymers

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model of polar polymers**

Yung, Yuk Sun, M.S.

San Jose State University, 1989

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**LIQUID CRYSTALS :
REFRACTIVE INDICES OF MONOMERS
AND DISCRETE MODEL OF POLAR POLYMERS**

**A Thesis
Presented to
The Faculty of the Department of Physics
San Jose State University**

**In Partial Fulfillment
of the Requirements for the Degree
Master of Science**

**By
Yuk Sun Yung
December 1989**

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ABSTRACT

In Part I, a brief introduction to liquid crystal monomers and polymers is given.

In Part II, the *ab initio* theory of linear and nonlinear optics of liquid crystals proposed recently by Lam et al. [Phys. Rev. A **37**, 3496 (1988)] is generalized to include three internal vector coordinates. One of these is the director and the other two represent electronic excitations. In addition to the frequency dependence, temperature dependence of dielectric constants and refractive indices is also derived by relating the macroscopic second order tensor to the molecular second order tensor. The result is compared with the experimental data on refractive indices measured by Mitra et al. [Liq. Cryst. **3**, 123 (1988)]. Good agreements with experiments are found.

In part III, the partition function of a simplified 2D discrete model of polar (liquid crystal) polymer proposed by Lam [Mol. Cryst. Liq. Cryst. **155**, 531 (1988)] is derived. The 2D model can easily be reduced to a 1D model by letting the width of the hairpin to be zero. In the 1D case, the exact solution of the partition function, the susceptibility and other properties are discussed in detail.

I . INTRODUCTION

1. INTRODUCTION TO LIQUID CRYSTALS

Liquid crystal¹⁻⁵ is a state of matter that is intermediate between the liquid state and the crystalline state. In the liquid crystalline state, the molecules are arranged in a three-dimensional periodic structure. In the liquid state, there is no structural order, and the molecules can move freely. Liquid crystals are not as ordered as crystals, but, also not as disordered as liquids. It is therefore possible to obtain liquid crystals in two different ways. The first way is to introduce degrees of freedom that are different from the positional order. For example, at low temperature range, the molecules of certain organic liquids that are made up of rod-like molecules tend to align preferably along one direction, commonly labelled by a unit vector $\mathbf{n}$, the so-called director. These anisotropic liquids are called nematic liquid crystals (Fig. 1) which are positionally disordered, but orientational ordered. The second way of obtaining liquid crystals is to impose one- or two-dimensional positional order rather than three-dimensional. For example, if one-dimensional positional order is introduced, the system can be viewed as a set of two-dimensional liquid layers stack on top of each other. These liquids are called smectic liquid crystals.

The main features of nematic liquid crystals are :

1. The centers of gravity of the molecules do not have long-range order, and hence there is no Bragg peak observed in the X-ray diffraction pattern. In fact, nematic liquid crystals flow like liquids. The viscosities of typical nematic liquid crystals are in the order of 0.1 Poise.
2. The molecules tend to align parallelly along one direction, labelled as the

director $\mathbf{n}$ which has inversion symmetry, i.e. the system behaves the same under $\mathbf{n}$ or $-\mathbf{n}$. If individual molecules carry a permanent electric dipole, there are just as many dipoles pointing up than there are dipoles pointing down.

3. The director $\mathbf{n}$ is arbitrary in space. In practice, $\mathbf{n}$ can be imposed by small forces such as a small external electric field or the guiding effects of the walls of the container.
4. Nematic phase is symmetry with respect to its mirror image. This means either the molecules are identical under their mirror images or the system consists of equal mixture of right- and left-handed molecules.

From the crystallographic point of view, properties 2 and 4 can be summarized by the symbol $D_{\infty h}$ under the Schonflies notation. This means that nematic liquid crystals are optically uniaxial and the optical axis is the director $\mathbf{n}$.

If chiral molecules, which are different from their mirror images, are dissolved into a nematic liquid crystal, the structure may undergo a helical distortion. The same distortion is found in cholesterol esters. Hence this helical phase is also called cholesteric (Fig.1). Locally, cholesteric is similar to nematic because molecules tend to align in a preferable direction labelled by the director $\mathbf{n}$. However, $\mathbf{n}$ is helical in cholesteric. If the z-axis is assigned as the helical axis, then the x, y, z components of $\mathbf{n}$ ($\equiv n_x\hat{x}+n_y\hat{y}+n_z\hat{z}$) will be given by

$$\begin{aligned} n_x &= \cos (q_0 z + \varnothing) , \\ n_y &= \sin (q_0 z + \varnothing) , \\ n_z &= 0 , \end{aligned} \tag{1.1}$$

where ϕ is arbitrary depending on where $z=0$ is chosen. Since $\mathbf{n}$ and $-\mathbf{n}$ are equivalent, the spatial period, L_p is given by $\pi/|q_0|$. Typical value of L_p is in the range of optical wavelengths; therefore, Bragg scattering can be observed with light beams. The sign of q_0 is also important; it distinguishes between right- and left-handed helices. At a given temperature, the same cholesteric always produces helices of the same sign. However, $q_0(T)$ may change sign at a certain temperature T^* . In this case, at $T=T^*$ the material behaves exactly like nematic liquid crystals.

Smectic liquid crystals have layered structure with a well-defined inter-layer spacing which can be measured by X-ray diffraction. There are two main types of smectics, the smectics A and C (Fig.1).

Smectic A liquid crystals are characterized by the following features :

1. They have layer structure and the layer spacing is close to the length of the molecules.
2. Each layer behaves like a two-dimensional liquid.
3. They are optically uniaxial. Each layer has the same director $\mathbf{n}$ which is also the optical axis, and is normal to the plane of the layers.
4. The normal to the layers is usually labelled as the z-axis. The directions z and $-z$ are equivalent.

Properties 3 and 4 can be summarized by the symbol D_∞ under the Schonflies notation.

Smectic C liquid crystals are characterized by the following features :

1. Each layer is still a two-dimensional liquid.
2. They are optically biaxial.

It can be seen that if the director n of each layer is tilted with respect to the normal of the layers, it will result in smectic C liquid crystals. There are other possible phases of liquid crystals, e.g. the smectic B and the exotic smectics.²⁻⁵

Liquid crystal polymers can be synthesized from the monomers.² They offer a new class of materials, which combine the anisotropic properties of liquid crystals and the properties of polymers. There are two common types of liquid crystal polymers, the main-chain polymers and the side-chain polymers (Fig. 2). Liquid crystal main-chain polymers offer outstanding mechanical properties, while liquid crystal side-chain polymers offer special optical properties that can be used in various optical applications. Polar liquid crystal polymers are made up of polar monomers. Both main-chain and side-chain polar polymers are possible.

The monomers in nematic liquid crystals can be easily oriented by a weak external electric field. Together with its anisotropic properties, nematic liquid crystals are commonly used in displays referred to as LCD's, such as wrist-watches and lap-top PC's. Smectic A liquid crystals are used in liquid crystal light valves (LCLVs) for the applications of color graphic terminals and the lithography for printed circuit board designs. Right now the resolution is in the order of 0.1 mm and there are active researches to bring the resolution down to μm range for the lithography applications in the processing of semiconductor devices. Research is also in process to apply smectic C liquid crystals to construct optical switches in the applications of optical communications. Liquid crystal polymers can be made into very light but very strong material, e.g. Kevlar, which is even stronger than steel. Important applications of liquid crystals are also found in many biological systems.⁵ Parts

of the brain and cell membranes are composed of organic molecules organized into liquid crystalline subunits. Studies of liquid crystals may eventually lead to a deeper understanding of living systems. Liquid crystals are therefore important in both pure and applied research.

II . REFRACTIVE INDICES OF NEMATIC MONOMERS

2. BACKGROUND OF PART II

For any electromagnetic wave propagating in an isotropic medium, e.g. air or water, the phase velocity is given by

$$v = \frac{1}{\sqrt{\epsilon\mu}} \quad , \quad (2.1)$$

where ϵ and μ are the permittivity and susceptibility of the medium. Eq. (2.1) may also be written as

$$v = \frac{c}{n} \quad , \quad (2.2)$$

where n is called the refractive index, and c ($\approx 3 \times 10^8$ m/s) is the velocity of light in vacuum

In an anisotropic medium, e.g. crystals, ϵ is in general a second order tensor. The velocity of light depends on its direction of polarization, and hence there is no single refractive index. It turns out that it is always possible to choose Ox , Oy , and Oz in such a way that the off-diagonal tensor elements vanish, leaving three principal refractive indices : n_1 , n_2 , n_3 . The three axes in this case are called the principal optical axes.

For a medium that has uniaxial symmetry, e.g. uniaxial nematic liquid crystals, two of the principal refractive indices are equal, e.g. $n_1=n_2$. In this case, Oz is called the optical axis, the director $\mathbf{n}$ in nematic liquid crystals. Usually the two principal refractive indices that are equal in magnitude are denoted by n_o

($=n_1=n_2$) and the remaining one is denoted by n_e ($=n_3$). The first one, n_o , is observed for an ordinary wave where the polarization is perpendicular to the optical axis. The second one, n_e , is observed for an extraordinary wave where the polarization is parallel to the optical axis. The subscripts $\perp$ and $\parallel$ are also commonly used for ordinary and extraordinary refractive indices, i.e. $n_o \equiv n_{\perp}$ and $n_e \equiv n_{\parallel}$.

Dielectric constants and refractive indices are important quantities characterizing materials. For liquid crystals in the nematic and the isotropic phases, there exist a few theoretical models on the polarizabilities and refractive indices.⁷⁻¹³ A brief summary was given in Ref. 14. In the usual approach in calculating the internal fields,¹⁵ some kind of cavity, for example a prolate spheroid, is assumed. The temperature variation of the refractive indices is obtained through the dependence on the order parameter. No discussion on the frequency dependence of the refractive indices was attempted. Furthermore, none of these models was found to be completely satisfactory when compared to experimental data. For example, according to Rao et al.,¹⁵ among the more realistic spheroidal models, the de Jeu-Bordewijk¹¹ and the Derzhanski-Petrov⁸ models give increasing optical anisotropy with increasing temperature which is anomalous. Meanwhile the Ibrahim-Haase model⁹ fails in its prediction of the isotropic refractive index.

In the *ab initio* theory of Lam, Ou-Yang and Lax,¹⁶ equations of motion for the material vector coordinates and the electromagnetic fields are derived from a Lagrangian coupled with a dissipative function. The former describes the reversible processes, and the latter takes care of irreversible processes such as dissipation. It is a purely deductive and consistent theory without the

use of any *ad hoc* cavity. In Ref. 16, apart from the center-of-mass coordinate of the molecule, two internal vector coordinates, one representing the director $\mathbf{n}$ (a unit vector) and the other representing an electronic excitation, are included.

An effective equation of motion for $\mathbf{n}$ describing optical reorientation of molecules is obtained. A new mechanism of the flexoelectric effect arising from induced dipoles is proposed. Frequency dependence of the dielectric constants and hence the refractive indices is derived. However, no temperature dependence of the dielectric constants is given.

In this work, the temperature dependence of the dielectric constants are derived by relating the macroscopic second order tensor to the molecular second order tensor. To obtain a better fit of the theoretical results for refractive indices with experiments,¹⁷ it is necessary to generalize the theory of Ref. 16 to include one more electronic coordinate. In Ch.3, the relationship between a general macroscopic tensor and the corresponding molecular tensor is derived. The case of liquid crystal is specified in Ch. 4. The equations of motion are given in Ch. 5 from which expressions for the refractive indices n_e and n_o are derived. The obtained results are compared with experimental data¹⁷ in Ch. 6. Ch. 7 concludes this part of the thesis with brief discussions.

---

3. GENERAL FORMULATION

A. Macroscopic Second Order Tensor

For a *general* macroscopic second order tensor χ_{ij} and the corresponding molecular second order tensor γ_{IJ} , one has¹⁸

$$\chi_{ij} = N_0 \langle \gamma_{IJ} \rangle_{ij}, \quad (3.1)$$

where N_0 is the number of molecules per unit volume. $\langle \gamma_{IJ} \rangle_{ij}$ is the ij -th component of the orientational ensemble average of the molecular tensor. The indices I, J refer to the molecular frame, and i, j to the laboratory frame. Here for uniaxial nematics

$$\langle \gamma_{IJ} \rangle_{ij} = \frac{1}{4\pi^2} \int_0^{2\pi} d\phi \int_0^{2\pi} d\psi \int_0^\pi \sin\theta d\theta \gamma_{IJ} a_{iI}(\phi, \psi, \theta) a_{jJ}(\phi, \psi, \theta) f(\cos^2\theta), \quad (3.2)$$

where $f(\cos^2\theta)$ is the orientational distribution function, a_{mM} are components of the rotation matrix that relates the molecular frame to the laboratory frame. In terms of the Eulerian angles (ϕ, ψ, θ) , (a_{mM}) is given by¹⁹

$$(a_{mM}) = \begin{pmatrix} \cos\phi\cos\psi - \cos\theta\sin\phi\sin\psi & \sin\phi\cos\psi + \cos\theta\cos\phi\sin\psi & \sin\theta\sin\psi \\ -\cos\phi\sin\psi - \cos\theta\sin\phi\cos\psi & -\sin\phi\sin\psi + \cos\theta\cos\phi\cos\psi & \sin\theta\cos\psi \\ \sin\theta\sin\phi & -\sin\theta\cos\phi & \cos\theta \end{pmatrix}. \quad (3.3)$$

Substituting (3.2) and (3.3) into (3.1), one gets

$$\begin{aligned} \chi_{11} = \chi_{22} &= \frac{N_0}{3} \left[(\gamma_{11} + \gamma_{22} + \gamma_{33}) + S \left(\frac{\gamma_{11} + \gamma_{22}}{2} - \gamma_{33} \right) \right] \equiv \alpha + \beta S \\ \chi_{33} &= \frac{N_0}{3} \left[(\gamma_{11} + \gamma_{22} + \gamma_{33}) - 2S \left(\frac{\gamma_{11} + \gamma_{22}}{2} - \gamma_{33} \right) \right] \equiv \alpha - 2\beta S \\ \chi_{ij} &= 0, i \neq j \end{aligned} \quad (3.4)$$

where S is the order parameter defined by

$$\begin{aligned} S &= \langle P_2(\cos\theta) \rangle = \int_0^\pi f(\cos^2\theta) P_2(\cos\theta) \sin\theta d\theta, \\ \text{and} \quad \alpha &\equiv \frac{N_0}{3} (\gamma_{11} + \gamma_{22} + \gamma_{33}), \\ \beta &\equiv \frac{N_0}{3} \left(\frac{\gamma_{11} + \gamma_{22}}{2} - \gamma_{33} \right) \end{aligned} \quad (3.5)$$

B. The Lagrangian

When all dissipative effects are absent, the Lagrangian describing the system of molecules and the electromagnetic field, in the continuum limit, is given by¹⁶

$$L = L_P + L_F + L_I, \quad (3.6)$$

Where

$$L_P = \int dX \left[\frac{1}{2} \sum_{\alpha=1}^N \rho^\alpha [\dot{x}^\alpha(X,t)]^2 - \rho^0 F(x^\beta(X,t), x^\beta_{,A}(X,t)) \right], \quad (3.7)$$

$$L_F = \int \frac{1}{2} \epsilon_0 [\mathbf{E}^2(\mathbf{z}, t) - c^2 \mathbf{B}^2(\mathbf{z}, t)] d\mathbf{z}, \quad (3.8)$$

$$L_I = \int [\mathbf{j}(\mathbf{z}, t) \cdot \mathbf{A}(\mathbf{z}, t) - q(\mathbf{z}, t) \Phi(\mathbf{z}, t)] d\mathbf{z}. \quad (3.9)$$

Here $\mathbf{x}^\alpha$ represents the position of the α -th particle in a spatial frame. N is the number of different particles, ions and electrons in a molecule in the case of liquid crystals. The quantity $\mathbf{X}$ is a continuum variable that designates a material point in the material frame and is a time-independent quantity. An overdot represents the material time derivative. ρ^α and q^α are respectively the mass and charge of the α -th particle divided by the average volume occupied by a molecule. $\rho^0 (\equiv \sum \rho^\alpha)$ is the mass density of the medium and $\rho^0 F$ the free energy per unit volume. $\mathbf{E}$ and $\mathbf{B}$ are the electric field and magnetic induction, respectively. $\mathbf{A}$ and Φ are the vector and scalar potentials. They are functions of position $\mathbf{z}$ in the spatial frame and are related to $\mathbf{E}$ and $\mathbf{B}$ by

$$\mathbf{E}(\mathbf{z}, t) \equiv -\nabla \Phi(\mathbf{z}, t) - \frac{\partial \mathbf{A}(\mathbf{z}, t)}{\partial t}, \quad (3.10)$$

$$\mathbf{B}(\mathbf{z}, t) \equiv \nabla \times \mathbf{A}(\mathbf{z}, t). \quad (3.11)$$

Charge and current densities are defined by

$$q(\mathbf{z}, t) \equiv \sum_{\alpha=1}^N q^\alpha \int \delta(\mathbf{z} - \mathbf{x}^\alpha(\mathbf{X}, t)) d\mathbf{X}, \quad (3.12)$$

$$\mathbf{j}(\mathbf{z}, t) \equiv \sum_{\alpha=1}^N q^\alpha \int \dot{\mathbf{x}}^\alpha(\mathbf{X}, t) \delta(\mathbf{z} - \mathbf{x}^\alpha(\mathbf{X}, t)) d\mathbf{X}, \quad (3.13)$$

and the mks unit is used.

In the absence of magnetic fields and ignoring any free charge, one has¹⁶

$$\mathbf{q} = -\nabla \cdot \mathbf{P} , \quad (3.14)$$

$$\mathbf{j} = \frac{\partial \mathbf{P}}{\partial t} + \nabla X(\mathbf{P} \times \dot{\mathbf{x}}) , \quad (3.15)$$

and

$$L_I = \int \mathbf{P} \cdot \mathbf{E} dz , \quad (3.16)$$

where $\mathbf{P}$ is the polarization per unit volume given by

$$\mathbf{P} = \sum_{\alpha=1}^N q_{\alpha}(\mathbf{x}_{\alpha} - \mathbf{x}) , \quad (3.17)$$

and $\mathbf{x}$ is the center-of-mass variable of the set of masses p^{α} .

4. LIQUID CRYSTALS

A. Molecule With Three Internal Coordinates

Let us consider a model of a molecule consisting of three internal vector coordinates (Fig. 3). For convenience, in the rest of Part I of the thesis, the superscript α , naming of the particles in Ch. 3, will be written as subscript, e.g., $\mathbf{x}^\alpha \rightarrow \mathbf{x}_\alpha$.

It is assumed that $q_3 = -q_1$ and $q_4 = -q_2$ for simplicity. For notational clarity, we let $\rho_1 \equiv m_1$, $\rho_2 \equiv m_2$, $\rho_3 \equiv \mu_1$ and $\rho_4 \equiv \mu_2$. Here m_i are much larger than μ_i . The center-of-mass coordinate $\mathbf{x}$ is given by

$$\mathbf{x} = (m_1 \mathbf{x}_1 + m_2 \mathbf{x}_2 + \mu_1 \mathbf{x}_3 + \mu_2 \mathbf{x}_4) / \rho_0, \quad (4.1)$$

where

$$\rho_0 = m_1 + m_2 + \mu_1 + \mu_2. \quad (4.2)$$

Define

$$\begin{aligned} \mathbf{n} &\equiv (\mathbf{x}_1 - \mathbf{x}_2) / l, & l &\equiv |\mathbf{x}_1 - \mathbf{x}_2|, \\ \mathbf{y}_1 &\equiv \mathbf{x}_3 - \mathbf{x}_1, \\ \mathbf{y}_2 &\equiv \mathbf{x}_4 - \mathbf{x}_2. \end{aligned} \quad (4.3)$$

Eqs (4.1) - (4.3) can be inverted to give

$$\mathbf{x}_1 = \mathbf{x} - \frac{\mu_1 \mathbf{y}_1 + \mu_2 \mathbf{y}_2}{\rho_0} + \frac{m_2 + \mu_2}{\rho_0} \mathbf{l}, \quad (4.4)$$

$$x_2 = x - \frac{\mu_1 y_1 + \mu_2 y_2}{\rho_0} - \frac{m_1 + \mu_1}{\rho_0} \ln , \quad (4.5)$$

$$x_3 = x - \frac{(\mu_1 - \rho_0) y_1 + \mu_2 y_2}{\rho_0} + \frac{m_2 + \mu_1}{\rho_0} \ln , \quad (4.6)$$

$$x_4 = x - \mu_1 y_1 + \frac{\mu_2 - \rho_0}{\rho_0} y_2 - \frac{m_1 + \mu_1}{\rho_0} \ln . \quad (4.7)$$

The kinetic energy per unit volume, K , can be expressed in terms of x and the three internal coordinates (n, y_1, y_2) as :

$$K \equiv \frac{1}{2} \sum_{\alpha=1}^4 m_{\alpha} \dot{x}_{\alpha}^2 \quad (4.8)$$

$$\begin{aligned} = \frac{1}{2} [& \rho_0 \dot{x}^2 + \frac{(m_2 + \mu_2)(m_1 + \mu_1)}{\rho_0} l^2 \dot{n}^2 + \frac{\mu_1(\rho_0 - \mu_1)}{\rho_0} \dot{y}_1^2 \\ & + \frac{\mu_2(\rho_0 - \mu_2)}{\rho_0} \dot{y}_2^2 - 2 \frac{\mu_1 \mu_2}{\rho_0} \dot{y}_1 \cdot \dot{y}_2 + \frac{2l\mu_1(m_2 + \mu_2)}{\rho_0} \dot{y}_1 \cdot \dot{n} \\ & - \frac{2l\mu_2(m_1 + \mu_1)}{\rho_0} \dot{y}_2 \cdot \dot{n}] . \end{aligned} \quad (4.9)$$

Similarly from (3.17), P can be expressed as

$$\begin{aligned} P &= \sum_{\alpha=1}^4 q_{\alpha} (x_{\alpha} - x) \\ &= -q_1 y_1 - q_2 y_2 , \end{aligned} \quad (4.10)$$

after simplification. The particular choice of the internal coordinates defined by (4.3) does not diagonalize the kinetic energy term, but it results in a simple expression of $\mathbf{P}$ which involves only $\mathbf{y}_1$ and $\mathbf{y}_2$, but not $\mathbf{n}$.

Following Ref. 16, we adopt the liquid-like hypothesis and assume

$$F = F(\rho_0, n_i, n_{i,j}, y_{1i}, y_{2i}) , \quad i, j = 1, 2, 3 \quad (4.11)$$

where $n_{i,j} \equiv \partial n_i / \partial z_j$.

B. Nematics

The usual nematic has local symmetry $D_{\infty h}$ with respect to the symmetry axis $\mathbf{n}$. When expanded to second order, F is given by

$$\begin{aligned} \rho_0 F = & \frac{a_1}{2} \mathbf{y}_1 \bullet \mathbf{y}_1 + \frac{a_2}{2} \mathbf{y}_2 \bullet \mathbf{y}_2 + a_3 \mathbf{y}_1 \bullet \mathbf{y}_2 + \frac{b_1}{2} (\mathbf{y}_1 \bullet \mathbf{n})^2 \\ & + \frac{b_2}{2} (\mathbf{y}_2 \bullet \mathbf{n})^2 + b_3 (\mathbf{y}_1 \bullet \mathbf{n})(\mathbf{y}_2 \bullet \mathbf{n}) + \mathbf{y}_1 \bullet [c_1 \mathbf{n}(\nabla \bullet \mathbf{n}) + c_2 (\mathbf{n} \bullet \nabla) \mathbf{n}] \\ & + \mathbf{y}_2 \bullet [d_1 \mathbf{n}(\nabla \bullet \mathbf{n}) + d_2 (\mathbf{n} \bullet \nabla) \mathbf{n}] + F_0(n_i, n_{i,j}) , \end{aligned} \quad (4.12)$$

where F_0 is the Oseen-Frank free energy density given by

$$F_0 = \frac{1}{2} K_1 (\nabla \bullet \mathbf{n})^2 + \frac{1}{2} K_2 (\mathbf{n} \bullet \nabla \mathbf{X} \mathbf{n})^2 + \frac{1}{2} K_3 (\mathbf{n} \mathbf{X} \nabla \mathbf{X} \mathbf{n})^2 , \quad (4.13)$$

where K_i 's are elastic constants. Higher order terms may be added to Eq. (4.12) as needed. In (4.12), the c_i and d_i terms correspond to flexoelectric effects.

The equations of motion for $\mathbf{n}$ and $\mathbf{y}_\mu$ ($\mu=1,2$) are the Lagrangian equations derived from (3.6) - (3.9), (3.16), (4.9) - (4.13). The equations governing $\mathbf{y}_\mu$ are given by

$$\begin{aligned} & \frac{\mu_1(\rho_0 - \mu_1)}{\rho_0} \frac{\partial^2 y_{1i}}{\partial t^2} - \frac{\mu_1 \mu_2}{\rho_0} \frac{\partial^2 y_{2i}}{\partial t^2} + \frac{I \mu_1 (m_2 + \mu_2)}{\rho_0} \frac{\partial^2 n_i}{\partial t^2} \\ & = -q_1 E_i - a_1 y_{1i} - a_3 y_{2i} - b_1 (\mathbf{y}_1 \bullet \mathbf{n}) n_i - b_3 (\mathbf{y}_2 \bullet \mathbf{n}) n_i \\ & \quad - c_1 n_i (\nabla \bullet \mathbf{n}) - c_2 (\mathbf{n} \bullet \nabla) n_i, \quad i=1,2,3, \end{aligned} \quad (4.14)$$

$$\begin{aligned} & \frac{\mu_2(\rho_0 - \mu_2)}{\rho_0} \frac{\partial^2 y_{2i}}{\partial t^2} - \frac{\mu_1 \mu_2}{\rho_0} \frac{\partial^2 y_{1i}}{\partial t^2} - \frac{I \mu_2 (m_1 + \mu_1)}{\rho_0} \frac{\partial^2 n_i}{\partial t^2} \\ & = -q_2 E_i - a_2 y_{2i} - a_3 y_{1i} - b_2 (\mathbf{y}_2 \bullet \mathbf{n}) n_i - b_3 (\mathbf{y}_1 \bullet \mathbf{n}) n_i \\ & \quad - d_1 n_i (\nabla \bullet \mathbf{n}) - d_2 (\mathbf{n} \bullet \nabla) n_i, \quad i=1,2,3. \end{aligned} \quad (4.15)$$

5. REFRACTIVE INDICES

A. Frequency Dependence of Dielectric Constants

Under the action of an oscillating field $E \sim \exp(-i\omega t)$ with optical angular frequency ω , it is an excellent approximation to allow y_μ to adiabatically follow $\mathbf{n}$. We therefore assume $\mathbf{n}$ is a constant and $y_\mu \sim \exp(-i\omega t)$. Ignoring the flexoelectric terms $\mathbf{n}(\nabla \cdot \mathbf{n})$ and $(\mathbf{n} \cdot \nabla)\mathbf{n}$ since they are much smaller in magnitude,⁵ (4.14) and (4.15) become

$$\left[a_1 - \frac{\mu_1(\rho_0 - \mu_1)}{\rho_0} \omega^2 + b_1(\mathbf{n}\mathbf{n}) \right] \mathbf{y}_1 + \left[a_3 + \frac{\mu_1\mu_2}{\rho_0} \omega^2 + b_3(\mathbf{n}\mathbf{n}) \right] \mathbf{y}_2 = -\mathbf{q}_1 \mathbf{E} , \quad (5.1)$$

$$\left[a_3 + \frac{\mu_1\mu_2}{\rho_0} \omega^2 + b_3(\mathbf{n}\mathbf{n}) \right] \mathbf{y}_1 + \left[a_2 - \frac{\mu_2(\rho_0 - \mu_2)}{\rho_0} \omega^2 + b_2(\mathbf{n}\mathbf{n}) \right] \mathbf{y}_2 = -\mathbf{q}_2 \mathbf{E} . \quad (5.2)$$

Solving (5.1) and (5.2), one gets

$$\mathbf{y}_1 = - [(\kappa_{\parallel})_1 \mathbf{n}\mathbf{n} + (\kappa_{\perp})_1 (\mathbb{I} - \mathbf{n}\mathbf{n})] \mathbf{E} , \quad (5.3)$$

$$\mathbf{y}_2 = - [(\kappa_{\parallel})_2 \mathbf{n}\mathbf{n} + (\kappa_{\perp})_2 (\mathbb{I} - \mathbf{n}\mathbf{n})] \mathbf{E} . \quad (5.4)$$

where

$$(\kappa_{\parallel})_1 \equiv - (A_3 q_2 - A_2 q_1) / (A_1 A_2 - A_3^2) ,$$

$$(\kappa_{\perp})_1 \equiv - (A_6 q_2 - A_5 q_1) / (A_4 A_5 - A_6^2) ,$$

$$(\kappa_{\parallel})_2 \equiv - (A_3 q_1 - A_1 q_2) / (A_1 A_2 - A_3^2) ,$$

$$\begin{aligned}
(\kappa_{\perp})_2 &\equiv - (A_6 q_1 - A_4 q_2) / (A_4 A_5 - A_6^2) , \\
A_1 &\equiv a_1 + b_1 - h_1 \omega^2 , \\
A_2 &\equiv a_2 + b_2 - h_2 \omega^2 , \\
A_3 &\equiv a_3 + b_3 + h_3 \omega^2 , \\
A_4 &\equiv a_1 - h_1 \omega^2 , \\
A_5 &\equiv a_2 - h_2 \omega^2 , \\
A_6 &\equiv a_3 + h_3 \omega^2 , \\
h_1 &\equiv \frac{\mu_1(\rho_0 - \mu_1)}{\rho_0} , \\
h_2 &\equiv \frac{\mu_2(\rho_0 - \mu_2)}{\rho_0} , \\
h_3 &\equiv \frac{\mu_2 \mu_2}{\rho_0} .
\end{aligned} \tag{5.5}$$

From (5.3), (5.4), and the definition of the dielectric constant κ_{ij} given by

$$P_i = \epsilon_0(\kappa_{ij} - \delta_{ij})E_j , \tag{5.6}$$

one obtains

$$\kappa_{ij} = \kappa_{\perp} \delta_{ij} + (\kappa_{\parallel} - \kappa_{\perp}) n_i n_j , \tag{5.7}$$

where

$$\kappa_{\perp}(\omega) = 1 + \frac{1}{\epsilon_0} \frac{A_5 q_1^2 + A_4 q_2^2 - 2A_6 q_1 q_2}{A_4 A_5 - A_6^2} , \tag{5.8}$$

$$\kappa_{||}(\omega) = 1 + \frac{1}{\epsilon_0} \frac{A_2 q_1^2 + A_1 q_2^2 - 2A_3 q_1 q_2}{A_1 A_2 - A_3^2} . \quad (5.9)$$

The frequency dependence on ω is contained in A_1 - A_6 . Here ϵ_0 is the permittivity constant.

B. Temperature Dependence of Dielectric Constants

To find the temperature dependence of the dielectric constants, let us take $\mathbf{n}$ to be in the $\mathbf{z}$ direction, rewrite (4.12) and ignoring the flexoelectric terms, one has

$$\rho_0 F = \chi_{ii}^{(1)} y_{1i} y_{1j} + \chi_{ii}^{(2)} y_{2i} y_{2j} + \chi_{ii}^{(3)} y_{1i} y_{2j} , \quad (5.10)$$

where

$$\begin{aligned} \chi_{11}^{(1)} &= \chi_{22}^{(1)} = \frac{a_1}{2} , \\ \chi_{33}^{(1)} &= \frac{a_1 + b_1}{2} , \\ \chi_{ij}^{(1)} &= 0 , i \neq j , \\ \chi_{11}^{(2)} &= \chi_{22}^{(2)} = \frac{a_2}{2} , \\ \chi_{33}^{(2)} &= \frac{a_2 + b_2}{2} , \\ \chi_{ij}^{(2)} &= 0 , i \neq j , \\ \chi_{11}^{(3)} &= \chi_{22}^{(3)} = a_3 , \\ \chi_{33}^{(3)} &= a_3 + b_3 , \\ \chi_{ij}^{(3)} &= 0 , i \neq j . \end{aligned} \quad (5.11)$$

Here a_1 - a_3 , b_1 - b_3 , and hence the $\chi_{ij}^{(3)}$ ($k=1,2,3$) are macroscopic second order tensors. Their temperature dependence are thus given by (3.4). In particular, $\chi_{11}^{(k)} = \alpha_k + \beta_k S$. By (3.4), (5.5) and (5.11) one gets

$$\begin{aligned}
 A_1 &\equiv 2\alpha_1 - 4\beta_1 S - h_1 \omega^2, \\
 A_2 &\equiv 2\alpha_2 - 4\beta_2 S - h_2 \omega^2, \\
 A_3 &\equiv \alpha_3 - 2\beta_3 S + h_3 \omega^2, \\
 A_4 &\equiv 2\alpha_1 + 2\beta_1 S - h_1 \omega^2, \\
 A_5 &\equiv 2\alpha_2 + 2\beta_2 S - h_2 \omega^2, \\
 A_6 &\equiv \alpha_3 + \beta_3 S + h_3 \omega^2.
 \end{aligned} \tag{5.12}$$

C. Frequency and Temperature Dependence of Refractive Indices

The refractive indices n_o and n_e are given by $n_o = (\kappa_{\perp})^{1/2}$ and $n_e = (\kappa_{\parallel})^{1/2}$. In terms of the order parameter S one has

$$\frac{1}{n_o^2 - 1} = \frac{D_1 S^2 + D_2 S + D_3}{S + D_4}, \tag{5.13}$$

$$\frac{1}{n_e^2 - 1} = \frac{-2D_1 S^2 + D_2 S - (D_3/2)}{S - (D_4/2)}, \tag{5.14}$$

where

$$\begin{aligned}
 D_1 &\equiv d_1, \\
 D_2 &\equiv d_2 (1/\lambda^2) + d_3, \\
 D_3 &\equiv d_4 (1/\lambda^4) + d_5 (1/\lambda^2) + d_6, \\
 D_4 &\equiv d_7 (1/\lambda^2) + d_8,
 \end{aligned} \tag{5.15}$$

and

$$\begin{aligned}
 d_1 &\equiv \epsilon_0 \left(\frac{4\beta_1\beta_2 - \beta_3^2}{2q_1^2\beta_2 + 2q_2^2\beta_1 - 2q_1q_2\beta_3} \right), \\
 d_2 &\equiv -8\pi^2c^2\epsilon_0 \left(\frac{h_1\beta_2 + h_2\beta_1 + h_3\beta_3}{2q_1^2\beta_2 + 2q_2^2\beta_1 - 2q_1q_2\beta_3} \right), \\
 d_3 &\equiv 2\epsilon_0 \left(\frac{2\alpha_1\beta_2 + 2\alpha_2\beta_1 - \alpha_3\beta_3}{2q_1^2\beta_2 + 2q_2^2\beta_1 - 2q_1q_2\beta_3} \right), \\
 d_4 &\equiv 16\pi^4c^4\epsilon_0 \left(\frac{h_1h_2 - h_3^2}{2q_1^2\beta_2 + 2q_2^2\beta_1 - 2q_1q_2\beta_3} \right), \\
 d_5 &\equiv -8\pi^2c^2\epsilon_0 \left(\frac{h_1\alpha_2 + h_2\alpha_1 + h_3\alpha_3}{2q_1^2\beta_2 + 2q_2^2\beta_1 - 2q_1q_2\beta_3} \right), \\
 d_6 &\equiv \epsilon_0 \left(\frac{4\alpha_1\alpha_2 - \alpha_3^2}{2q_1^2\beta_2 + 2q_2^2\beta_1 - 2q_1q_2\beta_3} \right), \\
 d_7 &\equiv -4\pi^2c^2 \left(\frac{q_1^2h_2 + 2q_2^2h_1 - 2q_1q_2h_3}{2q_1^2\beta_2 + 2q_2^2\beta_1 - 2q_1q_2\beta_3} \right), \\
 d_8 &\equiv 2 \left(\frac{q_1^2\alpha_2 + q_2^2\alpha_1 - q_1q_2\alpha_3}{2q_1^2\beta_2 + 2q_2^2\beta_1 - 2q_1q_2\beta_3} \right).
 \end{aligned} \tag{5.16}$$

Here λ is the optical wavelength in vacuum given by $\lambda = 2\pi c/\omega$, and c is the velocity of light in vacuum. Equivalently, one can express the refractive indices as

$$\frac{1}{n_o^2 - 1} = \frac{d_4 (1/\lambda^4) + (d_5 + d_2 S)(1/\lambda^2) + (d_6 + d_3 S + d_1 S^2)}{d_7 (1/\lambda^2) + (d_8 + S)}, \tag{5.17}$$

$$\frac{1}{n_e^2 - 1} = \frac{-\frac{d_4}{2}(1/\lambda^4) - (\frac{d_5}{2} - d_2 S)(1/\lambda^2) - (\frac{d_6}{2} - d_3 S + 2d_1 S^2)}{-\frac{d_7}{2}(1/\lambda^2) - (\frac{d_8}{2} - S)}. \tag{5.18}$$

Note that n_o and n_e are functions of S and λ^{-2} with eight parameters, d_1 - d_8 . The values of d_1 - d_8 can be determined from experiments.

6. COMPARISONS WITH EXPERIMENTS

Eqs. (5.17) and (5.18) are used to compare with experimental data¹⁷ for p-ethoxyphenyl trans-4-butyl cyclohexane carboxylate (EPBCC). The refractive indices n_o and n_e are functions of two variables, S and λ^2 , with eight parameters d_1 - d_8 . Specifically, we first use the experimental data of $n_o(T, \lambda)$, $n_e(T, \lambda)$ and $S(T)$ to find D_1 - D_4 as shown in (5.13) and (5.14) for each fixed λ using the Levenberg-Marquardt method²⁰ of least squares fitting. Here T is the temperature. The Levenberg-Marquardt method is an iteration method using a mixture of the inverse-Hessian method and the steepest descent method. It is used because n_o and n_e do not depend on D_1 - D_4 linearly. Since it is an iteration method, a set of initial values of D_1 - D_4 are needed to start the algorithm. From Appendix B, to a good approximation, $(n_o^2 - 1)^{-1}$ and $(n_e^2 - 1)^{-1}$ are linear functions of S . Therefore, for the initial values of D_1 - D_4 , we assume $D_3=D_4=0$, and assume D_1 and D_2 as the averages of D_1' and D_2' (B.10) determined by the straight lines passing through the two extreme points of the refractive indices. Take an example, for $\lambda = 6907 \text{ \AA}$,

$$\text{at } S = 0.3477, n_o = 1.461 \text{ and } n_e = 1.507;$$

$$\text{at } S = 0.6467, n_o = 1.454 \text{ and } n_e = 1.539.$$

If we assume $(n_o^2 - 1)^{-1}$ and $(n_e^2 - 1)^{-1}$ are linear function of S , we get

$$\frac{1}{n_o^2 - 1} = D_1'S + D_2' = (0.0542)S + (0.8626), \quad (6.1)$$

$$\frac{1}{n_e^2 - 1} = -2D_1'S + D_2' = -2(0.0938)S + (0.8520). \quad (6.2)$$

Hence for $\lambda = 6907 \text{ \AA}$, the initial values of D_1 - D_4 are assumed to be :

$$D_1 = 0.0740, D_2 = 0.8573, D_3 = D_4 = 0.$$

The same way is repeated for $\lambda = 5780 \text{ \AA}$, $5461 \text{ \AA}$ and $4758 \text{ \AA}$ to find the initial values of D_1 - D_4 . The final values of the four sets of D_1 - D_4 obtained from the Levenberg-Marquardt method are listed in Table I.

Table I. The parameters D_1 - D_4 as determined from experimental data.

	6907 $\text{\AA}$	5780 $\text{\AA}$	5461 $\text{\AA}$	4758 $\text{\AA}$
D_1	0.08403	0.08294	0.08111	0.07619
D_2	0.8264	0.8175	0.8080	0.7823
D_3	-0.1776	-0.1704	-0.1655	-0.1624
D_4	-0.2117	-0.2050	-0.2015	-0.2044

Since D_1 - D_4 are linear functions of d_1 - d_8 as shown in (5.19). Once the four sets of D_1 - D_4 are found, d_1 - d_8 can be determined easily using the least squares fitting to fit D_1 - D_4 as functions of λ^{-2} with parameters d_1 - d_8 . If the unit used for λ is 10^{-7} m , the result gives :

$$\begin{aligned}
 D_1 &= 0.081, \\
 D_2 &= -1.94 (1/\lambda^2) + 0.8709, \\
 D_3 &= -20.37 (1/\lambda^2)^2 + 2.00 (1/\lambda^2) - 0.2107, \\
 D_4 &= 0.315 (1/\lambda^2) - 0.216.
 \end{aligned} \tag{6.3}$$

Therefore, the values of d_1 - d_8 obtained for EPBCC are :

$$\begin{aligned} d_1 &= 0.081, d_2 = -1.94, d_3 = 0.8709, d_4 = -20.37, \\ d_5 &= 2.00, d_6 = -0.2107, d_7 = 0.315, d_8 = -0.216. \end{aligned} \quad (6.4)$$

The expressions (5.17) and (5.18) with the parameters d_1 - d_8 given by (6.1) are plotted as solid lines in Fig. 4. The result shows a pretty good agreement between the theoretical expressions and the experimental data. A listing of the Fortran program of the Levenberg-Marquardt method used in this chapter is shown in Appendix A. The resonance wavelengths can also be determined after d_1 - d_8 are found. For example, at $T = 74^\circ\text{C}$, $S = 0.348$, and the resonance wavelengths are $5080 \text{ \AA}$ for the ordinary wave and $3720 \text{ \AA}$ for the extraordinary wave.

7. DISCUSSION AND CONCLUSION OF PART II

In our work, an *ab initio* theory is used to derive the dielectric constants of nematic liquid crystals. The results give both temperature and wavelength dependence of dielectric constants and they agree pretty well with experimental data.

Other theories⁸⁻¹³ do not derive the frequency dependence of dielectric constants. In addition, most of them express n_o^2 and n_e^2 as linear functions of S . For example, the Vuks' model⁷ gives

$$\begin{aligned}\frac{4}{3} \pi N \alpha_e &= \frac{n_e^2 - 1}{\bar{n}^2 + 2}, \\ \frac{4}{3} \pi N \alpha_o &= \frac{n_o^2 - 1}{\bar{n}^2 + 2}, \\ \bar{n}^2 &\equiv \frac{n_e^2 + 2n_o^2}{3},\end{aligned}\tag{7.1}$$

where N is the number of molecules per unit volume, α_e and α_o are the molecular extraordinary and ordinary polarizabilities given by

$$\begin{aligned}\alpha_e &= \bar{\alpha} - \frac{2S}{3}(\alpha_{\perp} - \alpha_{\parallel}), \\ \alpha_o &= \bar{\alpha} + \frac{S}{3}(\alpha_{\perp} - \alpha_{\parallel}), \\ \bar{\alpha} &\equiv \frac{2\alpha_{\perp} + \alpha_{\parallel}}{3},\end{aligned}\tag{7.2}$$

where $\alpha_{\perp}$ and $\alpha_{\parallel}$ are the polarizabilities of a molecule perpendicular and parallel to the long molecular axis. Solving (7.1) and (7.2), one has :

$$\begin{aligned}
n_e^2 - 1 &= \frac{4\pi N[3\tilde{\alpha} - 2S(\alpha_{\perp} - \alpha_{\parallel})]}{3 - 4\tilde{\alpha}} , \\
n_o^2 - 1 &= \frac{4\pi N[3\tilde{\alpha} + S(\alpha_{\perp} - \alpha_{\parallel})]}{3 - 4\tilde{\alpha}} ,
\end{aligned} \tag{7.3}$$

By representing the molecules by an anisotropic homogeneously polarizable spheroid in an anisotropic continuum, de Jeu and Bordewijk¹¹ derive the following expressions,

$$\begin{aligned}
n_e^2 - 1 &= \frac{4}{3} \pi N \left[\frac{\alpha_{\parallel} (1+2S)}{1 - 4\pi N \alpha_{\parallel} A_{\parallel}} + \frac{\alpha_{\perp} (2-2S)}{1 - 4\pi N \alpha_{\perp} A_{\perp}} \right] , \\
n_o^2 - 1 &= \frac{4}{3} \pi N \left[\frac{\alpha_{\parallel} (1-S)}{1 - 4\pi N \alpha_{\parallel} A_{\parallel}} + \frac{\alpha_{\perp} (2+S)}{1 - 4\pi N \alpha_{\perp} A_{\perp}} \right] .
\end{aligned} \tag{7.4}$$

Ibrahim and Haase⁹ come up with similar expressions,

$$\begin{aligned}
n_e^2 - 1 &= \frac{4}{3} \pi N \left[\frac{g_{\parallel} \alpha_{\parallel} (1+2S)}{1 - r_{\parallel} \alpha_{\parallel}} + \frac{g_{\perp} \alpha_{\perp} (2-2S)}{1 - r_{\perp} \alpha_{\perp}} \right] , \\
n_o^2 - 1 &= \frac{4}{3} \pi N \left[\frac{g_{\parallel} \alpha_{\parallel} (1-2S)}{1 - r_{\parallel} \alpha_{\parallel}} + \frac{g_{\perp} \alpha_{\perp} (2+2S)}{1 - r_{\perp} \alpha_{\perp}} \right] .
\end{aligned} \tag{7.5}$$

In contrast, our result for n_o^2 and n_e^2 in (5.13) and (5.14) are not linear in S .

If the model of this work is modified to use only two internal vector coordinates, it can be shown that $(n_e^2 - 1)^{-1}$ and $(n_o^2 - 1)^{-1}$ vary linearly with S (Appendix B) as given by

$$\frac{1}{n_o^2 - 1} = D'_1 S + D'_2 ,$$

$$\frac{1}{n_e^2 - 1} = -2D'_1 + D'_2 . \quad (7.6)$$

As shown in Fig. 4, $(n_e^2 - 1)^{-1}$ and $(n_o^2 - 1)^{-1}$ are very close to st. lines with respect to S . However, the st. lines fittings become poor if we try to find D'_1 and D'_2 that satisfy both expressions of (7.6). This is the main reason that we expand to three internal vector coordinates in this work so that we can have a better agreement between the theory and the experimental data. To check the other theories against the experimental data, n_o^2 and n_e^2 are plotted against S as shown in Fig. 5. To a rough approximation, it is possible to fit n_o^2 and n_e^2 as independent straight lines with respect to S . However, if we try to satisfy the relationship between the slopes and interceptions of the two straight lines, it then becomes impossible to fit n_o^2 and n_e^2 as straight lines with respect to S .

As mentioned by Lam et al.,¹⁶ the method used here can be modified to include the motion of the center-of-mass variable; hence it is possible to discuss the phenomena of acoustic properties of liquid crystals. In the presence of magnetic fields, the magnetic dipole terms have to be included.

The formalism described in this work is equally applicable to dielectric liquids and ferrofluids.²¹

III. DISCRETE MODEL OF POLAR POLYMERS

8. BACKGROUND OF PART III

A. Partition Function

From the basic principle of statistical mechanics,²² if a system in equilibrium can be in one of N states, the probability of the system in the i th state with energy E_i is given by

$$P(E_i) = \frac{1}{Q} \exp(-\beta E_i) , \quad (8.1)$$

where
$$Q = \sum_{i=1}^N \exp(-\beta E_i) , \quad (8.2)$$

$$\beta \equiv \frac{1}{k_B T} , \quad (8.3)$$

k_B is the Boltzmann's constant and T is the temperature. The quantity Q in (8.1) is called the partition function from which all other thermodynamics properties can be derived. For example,

$$\begin{aligned} A &\equiv -\frac{1}{\beta} \ln Q , & P &\equiv -\left(\frac{\partial A}{\partial V}\right)_T , & S &\equiv -\left(\frac{\partial A}{\partial T}\right)_V , \\ G &\equiv A + PV , & U &\equiv A + TS , \end{aligned} \quad (8.4)$$

where A is the Helmholtz free energy, P is the pressure, V is the volume, S is the entropy, G is the Gibbs free energy, and U is the internal energy.

B. The Discrete Model of Polar Main-Chain

As proposed by Lam,²³ a possible model describing the conformation of a polar main-chain in an external electric field $\mathbf{E}$ is shown in Fig. 6. The length of each monomer is b and the length of the chain is Lb . This model assumes a biased random walk of the L repeated monomers such that the energy for a monomer parallel (antiparallel) to $\mathbf{E}$ causes energy $-\mu E$ (μE) where μ is the dipole moment of each monomer. A monomer perpendicular to $\mathbf{E}$ causes zero energy. Each bending from parallel to antiparallel, or vice versa, is called a hairpin which caused energy h . A pair of parallel (antiparallel) adjacent monomers have energy γ ($-\gamma$). All μ , γ , γ' and h are positive. The lattice is 3D in general, but also can be reduced to 2D or 1D for simplicity, or in special cases.

Nobody has solved this model analytically yet. However it can be solved easily by computer simulation, e.g. by the Monte Carlo method. In the 1D continuum limit and for $E=0$, the model reduces to that of Zwanzig and Lauritzen²⁴ which was solved exactly in the limit of $L \rightarrow \infty$. That solution showed a second-order phase transition with the number of hairpins acting as the order parameter. For $E \neq 0$ and $\gamma = \gamma' = 0$, in the continuum limit, the model reduces to that of Gunn and Warner²⁵ which was also solved exactly, but did not show any phase transition. As pointed out by Lauritzen and Zwanzig,²⁶ the continuum version of a physically discrete model may contain spurious results.

9. THE 2D DISCRETE MODEL

In order to solve the model analytically, the model is reduced to a simplified 2D (or 1D) version as shown in Fig. 7. This version allows the bending to go in one direction only. To further simplify the model, the interaction between the monomers are assumed to be negligible, i.e. we assume $\gamma=\gamma'=0$.

The partition function of the polar (liquid crystal) polymer is given by

$$Q(L,E) = Q_A(L,E) + Q_B(L,E) + Q_C(L,E) + Q_D(L,E) \quad , \quad (9.1)$$

where Q_A, Q_B, Q_C, Q_D are calculated from the four cases shown in Fig. 8,

$$\begin{aligned} Q_A(L,E) &= \sum_{N=1}^{\infty} \sum_{X_1=1}^{\infty} \cdots \sum_{X_N=1}^{\infty} \sum_{Y_1=1}^{\infty} \cdots \sum_{Y_N=1}^{\infty} \delta_{L, \sum X_j + \sum Y_j + (2N-1)q} \exp(-\beta U_A), \\ Q_B(L,E) &= \sum_{N=1}^{\infty} \sum_{X_1=1}^{\infty} \cdots \sum_{X_N=1}^{\infty} \sum_{Y_1=1}^{\infty} \cdots \sum_{Y_N=1}^{\infty} \delta_{L, \sum X_j + \sum Y_j + (2N-1)q} \exp(-\beta U_B), \\ Q_C(L,E) &= \sum_{N=1}^{\infty} \sum_{X_1=1}^{\infty} \cdots \sum_{X_{N+1}=1}^{\infty} \sum_{Y_1=1}^{\infty} \cdots \sum_{Y_N=1}^{\infty} \delta_{L, \sum X_j + \sum Y_j + 2Nq} \exp(-\beta U_C), \\ Q_D(L,E) &= \sum_{N=1}^{\infty} \sum_{X_1=1}^{\infty} \cdots \sum_{X_{N+1}=1}^{\infty} \sum_{Y_1=1}^{\infty} \cdots \sum_{Y_N=1}^{\infty} \delta_{L, \sum X_j + \sum Y_j + 2Nq} \exp(-\beta U_D) \quad , \end{aligned} \quad (9.2)$$

and

$$\begin{aligned} U_A &= (2N-1)h - \mu E(\sum X_j - \sum Y_j) \quad , \\ U_B &= (2N-1)h - \mu E(-\sum X_j + \sum Y_j) \quad , \\ U_C &= 2Nh - \mu E(\sum X_j - \sum Y_j) \quad , \\ U_D &= 2Nh - \mu E(-\sum X_j + \sum Y_j) \quad . \end{aligned} \quad (9.3)$$

Here X_i is the i th segment that the dipoles are pointing up, and Y_i is the i th segment that the dipoles are pointing down. In case A and B, there are $N+1$ segments that are pointing up and N segments that are pointing down, therefore there are $(2N-1)$ hairpins. In case C and D, there are equal ($=N$) segments pointing up and down, therefore there are $2N$ hairpins.

From (9.2) and (9.3), it is clear that

$$Q_B(L,E) = Q_A(L,-E) \text{ and } Q_D(L,E) = Q_C(L,-E) \quad . \quad (9.4)$$

Therefore, (9.1) becomes

$$Q(L,E) = Q_A(L,E) + Q_A(L,-E) + Q_C(L,E) + Q_C(L,-E) \quad . \quad (9.5)$$

From Appendix C, one obtains

$$\begin{aligned} Q_A(L,E) &= Q_A(L,E) = \frac{f}{(L-q-2)!} \lim_{z \rightarrow 0} \frac{d^{L-q-2}}{dz^{L-q-2}} \left[\frac{1}{F(z)} \right] , \\ Q_C(L,E) &= \frac{e^{u_0}}{(L-1)!} \lim_{z \rightarrow 0} \frac{d^{L-1}}{dz^{L-1}} \left[\frac{1}{F(z)} \right] - \frac{1}{(L-2)!} \lim_{z \rightarrow 0} \frac{d^{L-2}}{dz^{L-2}} \left[\frac{1}{F(z)} \right] , \\ Q_C(L,-E) &= \frac{e^{-u_0}}{(L-1)!} \lim_{z \rightarrow 0} \frac{d^{L-1}}{dz^{L-1}} \left[\frac{1}{F(z)} \right] - \frac{1}{(L-2)!} \lim_{z \rightarrow 0} \frac{d^{L-2}}{dz^{L-2}} \left[\frac{1}{F(z)} \right] . \end{aligned} \quad (9.6)$$

where

$$f \equiv e^{-\beta h}, \quad u_0 \equiv \mu \beta E \quad (9.7)$$

$$\text{and} \quad F(z) \equiv z^2 - 2 \cosh(u_0) z + 1 - f^2 z^{2(q+1)} . \quad (9.8)$$

Therefore (9.5) can be written as,

$$Q(L,E) = 2 [H_L - \cosh(u_0) H_{L-1} + f H_{L-q-2}] \quad , \quad (9.9)$$

where

$$H_m \equiv \lim_{z \rightarrow 0} \frac{d^m}{dz^m} \left[\frac{1}{F(z)} \right] \quad . \quad (9.10)$$

In General, $F(z) = 0$ is a $2(q+1)$ th order algebraic equation which can be solve exactly if $2(q+1) \leq 4$. Therefore $F(z)$ can only be solve exactly, and $Q(L,E)$ can only be expressed analytically for $q \leq 1$.

10. THE 1D CASE

If q is set to zero, the 2D model reduces to a 1D model. The partition function for the 1D model is given by,

$$Q = \frac{2}{(1-f^2)(z_2-z_1)} \left[\cosh(u_0) \left(\frac{1}{z_1^L} - \frac{1}{z_2^L} \right) + (f-1) \left(\frac{1}{z_1^{L-1}} - \frac{1}{z_2^{L-1}} \right) \right], \quad (10.1)$$

where

$$z_{2,1} = \frac{\cosh(u_0) \pm \sqrt{\cosh^2(u_0) - (1-f^2)}}{1-f^2}. \quad (10.2)$$

For $E=0$, the Helmholtz free energy A , and the average number of hairpins, $\bar{\pi}$ are given by

$$A \equiv -\frac{1}{\beta} \ln Q = -\frac{1}{\beta} [\ln 2 + (L-1) \ln(1+f)], \quad (10.3)$$

$$\bar{\pi} = \frac{\partial A}{\partial h} = \frac{(L-1)f}{1+f}. \quad (10.4)$$

Therefore the average number of hairpins increases monotonically from 0 to $(L-1)/2$ as temperature T increases from zero to infinity. This means that the polymer will bend more often when temperature increases.

The susceptibility χ is defined as $\partial P / \partial E$, where P is the polarization given by

$$P \equiv -\frac{\partial A}{\partial E} = L\mu \sinh(u_0) [\sinh^2(u_0) + \exp(-2\beta h)]^{-1/2}. \quad (10.5)$$

Therefore χ is given by

$$\chi = L\mu^2\beta \cosh(u_0) [\sinh^2(u_0) + \exp(-2\beta h)]^{-1/2} - L\mu^2\beta \cosh(u_0) \sinh^2(u_0) [\sinh^2(u_0) + \exp(-2\beta h)]^{-3/2}. \quad (10.6)$$

As $E \rightarrow 0$, we have $u_0 \rightarrow 0$, $\cosh(u_0) \rightarrow 1$ and $\sinh(u_0) \rightarrow 0$. This implies

$$\chi \rightarrow L\mu^2\beta \exp(\beta h), \quad (10.7)$$

which is identical to Eq. (5) of Gunn and Warner²⁵ if I there is identified as b in our model. The 1D model result can also be obtained by mapping the model to the 1D Ising model as shown in Appendix D.

11. DISCUSSION AND CONCLUSION OF PART III

$F(z) = 0$, where $F(z)$ is given in (9.8), is an algebraic equation of order $2(q+1)$ for $q \geq 0$. Since exact solution exists for an algebraic equation of order four or less; therefore roots of $F(z)$ can be expressed exactly for $q \leq 1$. This implies that the partition function Q can be expressed exactly in a 2D case for $q = 1$ besides the 1D case solved in Ch. 10.

The assumption that $\gamma = \gamma' = 0$ means that the interactions among molecules are ignored and the result shows no phase transition. The influence of other molecules on a single molecule can be treated using the mean-field method. The same formulation described in Ch. 9 can be used simply by replacing E with $E + aP$, where a is a proportional constant and P is the Polarization. In this way the solution will show phase transition. This is confirmed by an alternative approach which maps the problem to a quantum mechanical differentiation equation.²⁷ The susceptibility χ is then modified drastically, e.g. at low temperature and in the limit of $E \rightarrow 0$. instead of (10.7), one has

$$\chi \sim \beta^{-1} \exp(c/\beta) , \quad c > 0 . \quad (11.1)$$

The discrete model presented here is a better model than the continuum model used in Ref. 25. In that continuum model, Q depends on an arbitrary parameter l which has to be related to a physical quantity separately. Note that l comes in as the "density of states factor" when the continuum limit is taken on a physically discrete model. In our discrete model, this difficulty is avoided.

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-

APPENDIX A. FORTRAN PROGRAM LISTING OF THE LEVENBERG-MARQUARDT METHOD

```

*****
*      Program to fit 2 sets of pts to the following equations *
*      (a(1)*s^2+a(2)*s+a(3))/(s+a(4)) *
*      (-2a(1)*s^2+a(2)*s-0.5a(3))/(s-0.5a(4)) *
*      using the Levenberg-Marquardt method *
*      where S is the order parameter of the liquid crystal *
*      by Yuk S. Yung      Rev 1.0      date : 4/28/89 *
*****
      Parameter (NMAX=10)
      COMMON A(NMAX),ALPH(NMAX,NMAX),BETA(NMAX),X(50),Y(50),Z(50)
      COMMON/COM1/ ATEMP(NMAX)
100  FORMAT (2I2)
101  FORMAT (10F6.0)
102  FORMAT (/1X,'THE VALUE OF X, Y AND Z ARE :',/)
103  FORMAT (/1X,'THE INITIAL ESTIMATIONS OF THE PARAMETERS ARE :',/)
104  FORMAT (1X,7E11.4)
105  FORMAT (/1X,'VALUES OF CHISQ AND CHISQN, CHISQ GT CHISQN',/)
106  FORMAT (/1X,'VALUES OF CHISQ AND CHISQN, CHISQ LE CHISQN',/)
110  FORMAT (/1X,'THE PARAMETERS ARE :')
39   READ (7,100) N,NP
*** N IS THE NUMBER OF PARAMETERS AND NP IS THE NUMBER OF DATA POINTS
      IF ((2*NP).LT.N) THEN
          PAUSE 'NO OF DATA POINTS IS LESS THAN NO. OF PARAMETERS'
      ELSE IF (N.LT.1) THEN
          STOP
      ENDIF
      READ (7,101) (X(I),I=1,NP)
      READ (7,101) (Y(I),I=1,NP)
      READ (7,101) (Z(I),I=1,NP)
      DO 57 I=1,NP
          Y(I) = 1./(Y(I)**2-1)
          Z(I) = 1./(Z(I)**2-1)
57
*** CALCULATE THE INITIAL ESTIMATIONS OF A(I)
      A(1) = ((Y(2)-Y(1))+(Z(2)-Z(1))/-2.)/2./(X(2)-X(1))
      A(2) = (X(2)*Y(1)-X(1)*Y(2)+X(2)*Z(1)-X(1)*Z(2))/2./(X(2)-X(1))
      A(3) = 0.
      A(4) = 0.
      WRITE (8,102)
      WRITE (8,104) (X(I),I=1,NP)
      WRITE (8,104) (Y(I),I=1,NP)
      WRITE (8,104) (Z(I),I=1,NP)
      WRITE (8,103)
      WRITE (8,104) (A(I),I=1,N)
      ALAMDA = 0.001
      CHISQ = 0.
      DO 12 I=1,N
          BETA(I) = 0.
          DO 12 J=1,N
12      ALPH(I,J) = 0.

```

```

*** INITIALIZE VALUES OF LAMDA, ALPH AND BETA
    III = 0
11    CALL SETUP(NP,N,CHISQ)
    DO 13 I=2,N
    DO 13 J=1,I-1
13    ALPH(I,J) = ALPH(J,I)
    DO 14 I=1,N
14    ALPH(I,I) = (1.0+ALAMDA)*ALPH(I,I)
    CALL GAUSS (ALPH,BETA,N)
    CALL CALCHISQN (CHISQN,N,NP)
27    IF (CHISQN.GE.CHISQ) THEN
        DELTA = (CHISQN-CHISQ)/CHISQ
*** DEBUG ***
        WRITE (8,106)
        WRITE (8,104) CHISQ, CHISQN, DELTA
*** END OF DEBUG ***
    IF (DELTA.LT.1E-30) GOTO 37
    DO 17 I=1,N
17    ALPH(I,I) = ALPH(I,I)*(1.0+ALAMDA*10.)/(1.0+ALAMDA)
        ALAMDA = ALAMDA*10.
        CALL GAUSS (ALPH, BETA, N)
        CALL CALCHISQN (CHISQN,N,NP)
        GOTO 27
    ENDIF
    DO 32 I=1,N
32    A(I) = ATEMP(I)
*** DEBUG ***
    WRITE (8,105)
    DELTA = (CHISQN-CHISQ)/CHISQ
    WRITE (8,104) CHISQ, CHISQN, DELTA
    WRITE (8,110)
    WRITE (8,104) (A(I),I=1,N)
*** END OF DEBUG ***
    IF (III.LT.200) THEN
        ALAMDA = ALAMDA/10.
        III = III+1
        CHISQ = 0.
        GOTO 11
    ENDIF
37    WRITE (8,110)
    WRITE (8,104) (A(I),I=1,N)
    DO 38 I=1,NP
    Y(I) = (A(1)*X(I)**2+A(2)*X(I)+A(3))/(X(I)+A(4))
38    Z(I) = (-2.*A(1)*X(I)**2+A(2)*X(I)-0.5*A(3))/(X(I)-0.5*A(4))
    WRITE (8,102)
    WRITE (8,104) (X(I),I=1,NP)
    WRITE (8,104) (Y(I),I=1,NP)
    WRITE (8,104) (Z(I),I=1,NP)
    GOTO 39
END
SUBROUTINE SETUP (NP,N,CHISQ)
PARAMETER (NMAX=10)
COMMON A(NMAX),ALPH(NMAX,NMAX),BETA(NMAX),X(50),Y(50),Z(50)
DIMENSION DYDA(NMAX),DZDA(NMAX)
DO 11 I=1,NP

```

```

XSQ = X(I)**2
XPA4 = X(I)+A(4)
XMHA4 = X(I)-0.5*A(4)
HA3 = A(3)+0.5
A1XSQ = A(1)*XSQ
A2X = A(2)*X(I)
YIMY = Y(I) - (A1XSQ+A2X+A(3))/XPA4
ZIMZ = Z(I) - (-2.*A1XSQ+A2X-HA3)/XMHA4
DYDA(1) = XSQ/XPA4
DZDA(1) = -2.*XSQ/XMHA4
DYDA(2) = X(I)/XPA4
DZDA(2) = X(I)/XMHA4
DYDA(3) = 1./XPA4
DZDA(3) = -0.5/XMHA4
DYDA(4) = -1.*(A1XSQ+A2X+A(3))/(XPA4**2)
DZDA(4) = 0.5*(-2.*A1XSQ+A2X-HA3)/(XMHA4**2)
CHISQ = CHISQ + YIMY**2 + ZIMZ**2
DO 12 II=1,N
  BETA(II) = BETA(II)+YIMY*DYDA(II)+ZIMZ*DZDA(II)
DO 12 J=II,N
  ALPH(II,J) = ALPH(II,J)+DYDA(II)*DYDA(J)+DZDA(II)*DZDA(J)
12 *** DEBUG ***
*   WRITE (8,100)
*   WRITE (8,101) YIMY,ZIMZ
*   WRITE (8,101) (DYDA(J),J=1,N)
*   WRITE (8,101) (DZDA(J),J=1,N)
*   WRITE (8,101) (BETA(J),J=1,N)
*   DO 13 II=1,N
*13  WRITE (8,101) (ALPH(II,J),J=1,N)
*100  FORMAT (/1X,'DEBUG YIMY, ZIMZ, DYDA, DZDA, BETA AND ALPH',/)
*101  FORMAT (1X,7E11.4)
*** END OF DEBUG ***
11  CONTINUE
    RETURN
    END
    SUBROUTINE GAUSS(B,Y,N)
*****
*   GAUSSIAN ELIMINATION WITH FULL PIVOTING TO SOLVE LINEAR *
*   LINEAR EQUATIONS      B * = Y *
*   THE INVERSE OF B WILL BE STORED IN A AND THE SOLUTION *
*   THE SOLUTION x IS RETURNED IN y *
*   P.28 OF NUMERICAL RECIPES *
*   12/23/88 *
*****
    PARAMETER (NMAX=10)
    DIMENSION B(NMAX,NMAX),Y(NMAX),IPIV(NMAX),A(NMAX,NMAX)
    DIMENSION INDXR(NMAX),INDXC(NMAX)
    DO 51 I=1,N
    DO 51 J=1,N
51  A(I,J) = B(I,J)
*** DEBUG ***
*   WRITE (8,100)
*   DO 61 I=1,N
*61  WRITE (8,101) (A(I,J),J=1,N)
*   WRITE (8,101) (Y(J),J=1,N)
*100  FORMAT (/1X,'DEBUG A AND Y IN GAUSS SUBROUTINE',/)

```

```

*101  FORMAT (1X,7E11.4)
*** END OF DEBUG ***
DO 11 J=1,N
  IPIV(J) = 0
11  CONTINUE
DO 22 I=1,N
  BIG=0.
DO 13 J=1,N
  IF (IPIV(J).NE.1) THEN
    DO 12 K=1,N
      IF (IPIV(K).EQ.0) THEN
        IF (ABS(A(J,K)).GE.BIG) THEN
          BIG = ABS(A(J,K))
          IROW = J
          ICOL = K
        ENDIF
      ELSE IF (IPIV(K).GT.1) THEN
        PAUSE 'SINGULAR MATRIX'
      ENDIF
    CONTINUE
12  ENDIF
13  CONTINUE
  IPIV(ICOL) = IPIV(ICOL)+1
  IF (IROW.NE.ICOL) THEN
    DO 14 L=1,N
      DUM = A(IROW,L)
      A(IROW,L) = A(ICOL,L)
      A(ICOL,L) = DUM
14  CONTINUE
      DUM = Y(IROW)
      Y(IROW) = Y(ICOL)
      Y(ICOL) = DUM
    ENDIF
    INDXR(I) = IROW
    INDXC(I) = ICOL
    IF (A(ICOL,ICOL).EQ.0) PAUSE 'SINGULAR MATRIX'
    PIVINV = 1./A(ICOL,ICOL)
    A(ICOL,ICOL) = 1.
    DO 16 L=1,N
      A(ICOL,L)=A(ICOL,L)*PIVINV
16  CONTINUE
      Y(ICOL) = Y(ICOL)*PIVINV
    DO 21 LL=1,N
      IF (LL.NE.ICOL) THEN
        DUM = A(LL,ICOL)
        A(LL,ICOL) = 0.
        DO 18 L=1,N
          A(LL,L) = A(LL,L)-A(ICOL,L)*DUM
18  CONTINUE
          Y(LL) = Y(LL)-Y(ICOL)*DUM
        ENDIF
      CONTINUE
21  CONTINUE
22  CONTINUE
    DO 24 L=N,1,-1
      IF (INDXR(L).NE.INDXC(L)) THEN
        DO 23 K=1,N

```



```

        DUM = A(K,INDXR(L))
        A(K,INDXR(L)) = A(K,INDXC(L))
        A(K,INDXC(L)) = DUM
23      CONTINUE
      ENDIF
24      CONTINUE
      RETURN
      END
      SUBROUTINE CALCHISON (CHISON,N,NP)
      PARAMETER (NMAX=10)
      COMMON A(NMAX),ALPH(NMAX,NMAX),BETA(NMAX),X(50),Y(50),Z(50)
      COMMON/COM1/ ATEMP(NMAX)
      CHISON = 0.
      DO 15 I=1,N
15      ATEMP(I) = A(I)+BETA(I)
      DO 16 I=1,NP
      XSQ=X(I)**2
      XPA4 = X(I) + ATEMP(4)
      XMHA4 = X(I)-0.5*ATEMP(4)
      HA3=0.5*ATEMP(3)
      A1XSQ = ATEMP(1)*XSQ
      A2X = ATEMP(2)*X(I)
      YIMY = Y(I)-(A1XSQ+A2X+ATEMP(3))/XPA4
      ZIMZ = Z(I)-(-2.*A1XSQ+A2X-HA3)/XMHA4
16      CHISON = CHISON+YIMY**2+ZIMZ**2
      RETURN

```

APPENDIX B. MOLECULE WITH TWO INTERNAL COORDINATES

Instead of a four-particle molecular model, a three-particle molecular model (Fig. 9) is used in Ref. 16. It is assumed that $\rho_1 \equiv m_1$, $\rho_2 \equiv m_2$, $\rho_3 \equiv \mu$ and $q_3 = -(q_1 + q_2)$. Following the same procedure described in Ch. 4, the center-of-mass coordinate $\mathbf{x}$ is given by

$$\mathbf{x} = (m_1 \mathbf{x}_1 + m_2 \mathbf{x}_2 + \mu \mathbf{x}_3) / \rho_0, \quad (\text{B.1})$$

where

$$\rho_0 = m_1 + m_2 + \mu. \quad (\text{B.2})$$

Define

$$\begin{aligned} \mathbf{n} &\equiv (\mathbf{x}_1 - \mathbf{x}_2) / l, & l &\equiv |\mathbf{x}_1 - \mathbf{x}_2|, \\ \mathbf{y} &\equiv \mathbf{x}_3 - \mathbf{x}_1. \end{aligned} \quad (\text{B.3})$$

Eqs. (B.1)-(B.3) can be inverted to give

$$\begin{aligned} \mathbf{x}_1 &= \mathbf{x} - \frac{\mu}{\rho_0} \mathbf{y} + \frac{m_2}{\rho_0} l \mathbf{n}, \\ \mathbf{x}_2 &= \mathbf{x} - \frac{\mu}{\rho_0} \mathbf{y} - \frac{m_1 + \mu}{\rho_0} l \mathbf{n}, \\ \mathbf{x}_3 &= \mathbf{x} + \frac{m_1 + m_2}{\rho_0} \mathbf{y} + \frac{m_2}{\rho_0} l \mathbf{n}, \end{aligned} \quad (\text{B.4})$$

The kinetic energy per unit volume, T , is now given by

$$T \equiv \frac{1}{2} \sum_{\alpha=1}^3 m_{\alpha} \dot{\mathbf{x}}_{\alpha}^2$$

$$\begin{aligned}
&= \frac{1}{2} \left[\rho_0 \dot{\mathbf{x}}^2 + \frac{m_2(m_1+\mu)}{\rho_0} |\dot{\mathbf{n}}|^2 + \frac{\mu(m_1+m_2)}{\rho_0} \dot{\mathbf{y}}^2 \right. \\
&\quad \left. + \frac{2m_2\mu}{\rho_0} |\dot{\mathbf{y}} \cdot \dot{\mathbf{n}}| \right] .
\end{aligned} \tag{B.5}$$

Similarly $\mathbf{P}$ can be expressed as

$$\begin{aligned}
\mathbf{P} &= \sum_{\alpha=1}^3 q_{\alpha} (\mathbf{x}_{\alpha} - \mathbf{x}) \\
&= - (q_1 - q_2) \mathbf{y} - q_2 \ln .
\end{aligned} \tag{B.6}$$

Ignoring the flexoelectric effects, the free energy per unit volume, $\rho_0 F$ is given by

$$\rho_0 F = \frac{a}{2} \mathbf{y} \cdot \mathbf{y} + \frac{b}{2} (\mathbf{y} \cdot \mathbf{n})^2 + F_0(n_i, n_{i,j}) , \tag{B.7}$$

where F_0 is the Oseen-Frank free energy. Following the same arguments described in Ch. 5, instead of (5.3), one gets

$$\left[a - \frac{\mu(m_1+m_2)}{\rho_0} \omega^2 + b(\mathbf{n}\mathbf{n}) \right] \mathbf{y} = - (q_1+q_2) \mathbf{E} . \tag{B.8}$$

Inverting (B.8), one has

$$\begin{aligned}
\mathbf{y} &= \frac{- (q_1+q_2)}{a + b - \mu(m_1+m_2)\omega^2/\rho_0} \mathbf{n}\mathbf{n} \\
&\quad + \frac{- (q_1+q_2)}{a - \mu(m_1+m_2)\omega^2/\rho_0} (\mathbf{1} - \mathbf{n}\mathbf{n})
\end{aligned} \tag{B.9}$$

Applying (3.4), (5.8), (5.9) and (B.9), one gets

$$\begin{aligned}\frac{1}{n_o^2-1} &= \frac{2\alpha + 2\beta S - \mu(m_1+m_2)\omega^2/\rho_0}{(q_1+q_2)^2} = D_1'S + D_2', \\ \frac{1}{n_e^2-1} &= \frac{2\alpha - 4\beta S - \mu(m_1+m_2)\omega^2/\rho_0}{(q_1+q_2)^2} = -2D_1'S + D_2',\end{aligned}\quad (B.10)$$

where

$$D_1' \equiv \frac{2\beta}{(q_1+q_2)^2}, \quad D_2' \equiv \frac{2\alpha - \mu(m_1+m_2)\omega^2/\rho_0}{(q_1+q_2)^2}. \quad (B.11)$$

Therefore, if we use a three-particle molecular model, then both $(n_o^2-1)^{-1}$ and $(n_e^2-1)^{-1}$ are linear functions of S and ω^2 (or λ^{-2}).

APPENDIX C : THE Z-TRANSFORM

To evaluate a function $Q(L)$ of a discrete L ($L \geq 0$), one can use the Z-transform that is analogous to using Laplace transform for a continuous variable. One first takes the Z-transform, sometimes called the generating function as :

$$G(z) = \sum_{L=0}^{\infty} z^L Q(L) \quad , \quad (C.1)$$

where z is a complex variable. Now it can be proved by Cauchy's residue theorem that

$$\int_C \frac{dz}{z^{L+1}} G(z) = (2\pi i) Q(L) \delta_{L,L} \quad , \quad (C.2)$$

where C is a simple closed path enclosed $z = 0$ and, $\delta_{L,L} = 1$, when $L = L$, $\delta_{L,L} = 0$, when $L \neq L$.

From (C.2), one can derive the inverse Z-transform and express the original function as :

$$Q(L) = \frac{1}{2\pi i} \int_C \frac{dz}{z^{L+1}} G(z) \quad . \quad (C.3)$$

APPENDIX D : THE 1D ISING MODEL APPROACH

For $q = 0$, the 1D model described in Sec. 10 can be mapped onto the 1D Ising model. This can be done by considering the up segments to be spin +1 and the down segments to be spin -1; parallel adjacent spins have energy zero and antiparallel adjacent spins have energy h . Then the partition function $Q(L,E)$ can be expressed as

$$Q(L,E) = \sum_{\sigma_1=-1}^1 \sum_{\sigma_2=-1}^1 \cdots \sum_{\sigma_L=-1}^1 \exp(\beta, \xi) , \quad (D.1)$$

where

$$\xi = -\frac{h}{2} \sum_{j=1}^{L-1} (\sigma_j \sigma_{j+1} - 1) - \mu E \sum_{j=1}^L \sigma_j . \quad (D.2)$$

Compare the expressions with Ref. 28, the partition function is equivalent to the free boundary partition function of the 1D Ising model with the following substitutions

$$\begin{aligned} \exp\left(-\frac{\beta h}{2} (L-1)\right) Z_{1,N}^F &\rightarrow Q(L,E) , \quad N \rightarrow L, \\ E_1 \rightarrow \frac{h}{2} , \quad H \rightarrow \mu E \equiv \frac{u_0}{\beta} . \end{aligned} \quad (D.3)$$

Applying the substitutions and (2.14) of Ref. 28, one gets

$$\begin{aligned} Q(L,E) &= \exp\left(-\frac{\beta h}{2} (L-1)\right) Z_{1,N}^F , \\ &= f^{(L-1)/2} \left[\lambda_+^{L-1} \{ \cosh u_0 + (\sinh^2 u_0 + f) (\sinh^2 u_0 + f^2)^{-1/2} \} \right] \end{aligned}$$

$$+ \lambda_{\pm}^{L-1} \{ \cosh u_0 - (\sinh^2 u_0 + f) (\sinh^2 u_0 + f^2)^{-1/2} \} , \quad (\text{D.4})$$

where $f \equiv \exp(-\beta h)$, and

$$\begin{aligned} \lambda_{\pm} &\equiv f^{-(1/2)} [\cosh u_0 \pm \sqrt{\sinh^2 u_0 + f^2}] , \\ &= f^{-(1/2)} [\cosh u_0 \pm \sqrt{\cosh^2 u_0 - (1 - f^2)}] . \end{aligned} \quad (\text{D.5})$$

Substituting (D.5) into (D.4), we can get the same expression (10.1) for $Q(L, E)$.

Fig. 1. Common Liquid Crystals

- (a) Nematic Liquid Crystal. $\mathbf{n}$ is the director.
- (b) Cholesteric Liquid Crystal. $\mathbf{n}$ is the director, and π/q_0 is the spatial period.
- (c) Smectic A Liquid Crystal. The director $\mathbf{n}$ and the normal of the layer are both at the z direction, d is the inter-layer spacing.
- (d) Smectic C Liquid Crystal. The director $\mathbf{n}$ is tilted at an angle ω with respect to z , the normal of the layer.

Fig. 2 Schematic representation of the chemical constitution of Liquid Crystal Polymers

(a) Liquid Crystal main-chain polymers

(b) Liquid Crystal side-chain polymers

Fig. 3. Molecule with three internal coordinates. n is the director, q_i 's are the charges associated with the particles, where q_1, q_2 are positive ions and q_3, q_4 are electronic charges.

Fig. 4. Comparisons of (5.17) and (5.18) with experimental data¹⁷ on EPBCC. The solid lines, $(n_0^{2-1})^{-1}$, and the broken lines, $(n_0^{2-1})^{-1}$, are the theoretical results of (5.17) and (5.18). The discrete points are experimental data : X for $\lambda = 6907\text{\AA}$, O for $\lambda = 5780\text{\AA}$, Δ for $\lambda = 5461\text{\AA}$, ∇ for $\lambda = 4758\text{\AA}$.

Fig. 5. Plotting of n_0^2 , n_θ^2 vs S for EPBCC,¹⁷ X for $\lambda = 6907\text{\AA}$ and ∇ for $\lambda = 4758\text{\AA}$. It is impossible to fit n_0^2 and n_θ^2 as straight lines with respect to S , and have slopes and intercepts satisfy (7.5), or (7.6), or (7.7). The solid lines are drawn to guide the eyes.

Fig. 6. The discrete model of polar main-chain polymers in an external electric field E . The lattice may be 1-3 D. A monomer parallel (antiparallel) to E causes energy $-\mu E$ (μE). A monomer perpendicular to E causes zero energy. Each bending from parallel to antiparallel, or vice versa, causes energy h .

Fig. 7. The simplified 2D (or 1D) model. q is a constant, and $q = 0$ reduces the model to 1D. Here the horizontal bonds are in one direction only.

Fig. 8. The four cases of the simplified 2D (or 1D) model of polar main-chain polymers. The diagram shown here corresponds to $N=2$.

- (a) Case A, first monomer up, last monomer down.
- (b) Case B, first monomer down, last monomer up.
- (c) Case C, first monomer up, last monomer up.
- (d) Case D, first monomer down, last monomer down.

Fig. 9. Molecule with two internal coordinates. n is the director, q_i 's are the charges associated with the particles, where q_1 , q_2 are positive ions and q_3 is the electronic charge.