Influence of Elastic Anisotropy on the Structure of Néel Inversion Walls in Liquid Crystal Polymers

Ding-Kuo Ding and Edwin L. Thomas*

Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received June 2, 1993; Revised Manuscript Received August 23, 1993•

ABSTRACT: A solution of the director orientation across Néel inversion walls in a liquid crystal placed in a magnetic field for different values of the elastic anisotropy is presented. The appropriate characteristic length, containing the bend, k_{33}, and splay, k_{11}, elastic constants, for Néel type inversion walls is redefined as $(1/H)\,[(k_{11}+k_{33})/\chi_a]^{1/2}$. The qualitative, and, in favorable cases, quantitative, values of the elastic anisotropy of a liquid crystal polymer can be obtained from the images through the direct measurements of the director field via a lamellar decoration technique.

Introduction

Liquid crystals are typically aligned via flow or electric or magnetic fields. Different types of inversion walls may be formed during field alignment.[1] Liquid crystal polymers also form inversion walls under an applied field.[2-4] The structure of inversion walls should be different for rigid-rod molecules as compared to flexible molecules. The bend elastic constant increases with the persistence length, and the splay constant is proportional to the chain length.[5] These two elastic constants are usually not the same, especially for liquid crystal polymers, where the splay constant is expected to be largest due to the long polymer chain.[6] Defect structures in liquid crystals depend dramatically on the values of elastic anisotropy, which is defined as $\epsilon = (k_{11} + k_{33})/(k_{11} + k_{33})$. However, the effect of elastic anisotropy on the structure of inversion walls has seldom been addressed in the literature[7,8] and up to now has not been reported for thermotropic liquid crystal polymers.

Liquid crystals, in general, are characterized by a vector called the director, **n** (here **n** and −**n** are equivalent), which indicates the locally preferred orientation of molecules. When a nematic liquid crystal of positive diamagnetic anisotropy is placed in a magnetic field, the director orients parallel to the field direction. Regions of uniform orientation along the field direction can be separated by an inversion wall, where the director orientation changes by an angle π on crossing the wall. These walls are analogous to the Bloch (twist) or the Néel (splay–bend) walls in spin systems.[9] They can terminate in disclinations of half integral strength or form loops.[2,10] The differential equation describing the director orientation across the inversion wall based on continuum theory[11] in the two-dimensional case has been derived by Helfrich[1] and solved for the equal elastic constant approximation. The thickness of the inversion wall is defined by a characteristic length $\xi = (1/H)(k/\chi_a)^{0.5}$, where H is the magnetic field strength, k is the Frank elastic constant, and χ_a is the magnetic susceptibility anisotropy. Although optical microscopy has been used to measure elastic anisotropy via the ellipiticity of a closed wall in small-molecule liquid crystals (SMLCs), because of low spatial resolution, this method offers little information about the detailed molecular orientation across the inversion walls.[7] The lamellar decoration technique permits high-resolution imaging of the director field via TEM,[12] SEM, or AFM. Through the measurement of the director field around a disclination, the value of elastic anisotropy may be obtained.[13] Some "average" elastic constants of main-chain thermotropic liquid crystal polymers were recently obtained from TEM and SEM utilizing lamellar decoration of the wall structure with the assumption of equal splay and bend constants.[2,4]

The present work concerns the influence of elastic anisotropy on the structure of Néel inversion walls. We present the numerical solutions for the director field across Néel inversion walls with elastic anisotropy. These solutions combined with the lamellar decoration technique of Thomas and Wood[12] permit quantitative measurement of the bend-to-splay elastic anisotropy. Knowledge of the magnetic susceptibility anisotropy allows the determination of absolute values of the elastic constants.

Equiconstant Néel Inversion Wall. In a thin film, the director may be confined to lie in the plane of the film. In this case, the director has only 1 degree of freedom, ϕ, the angle with respect to some fixed axis contained in the plane. Assuming the field[14] is along the z direction and the director is confined to the zx plane, a bend–splay (Néel bend) wall parallel to the field and a splay–bend (Néel splay) wall normal to the field may be formed (see Figure 1). If the director, ϕ, is a function of x only, the equilibrium nonlinear differential equation of Néel bend (bend–splay) wall is given by[1]

$$\chi_a H^2 \sin\phi\cos\phi - k_{11}\cos\phi\frac{d}{dx}\left(\cos\phi\frac{d\phi}{dx}\right) - k_{33}\sin\phi\frac{d}{dx}\left(\sin\phi\frac{d\phi}{dx}\right) = 0 \quad (1)$$

For the equal elastic constant approximation, $k_{11} = k_{33} = k$, the equation simplifies to

$$\chi_a H^2 \sin\phi\cos\phi - k_{11}\frac{d^2\phi}{dx^2} = 0$$

which can be solved subject to the boundary conditions,

$$\phi(x=-\infty) = 0,\quad \phi(x=+\infty) = \pm\pi,\quad \frac{d\phi}{dx}(x=-\infty) = \frac{d\phi}{dx}(x=+\infty) = 0$$

The solution first obtained by Helfrich is $\phi = 2\tan^{-1}(\exp(\pm x/\xi))$, where ξ is the characteristic length and equal to $(1/H)(k_{11}/\chi_a)^{0.5}$ and 2ξ is a measure of the wall thickness. In the general case, the quantitative director orientation across the inversion wall with different values of the bend and splay constants has not been reported yet.

• Abstract published in *Advance ACS Abstracts*, October 15, 1993.

0024-9297/93/2226-6531$04.00/0

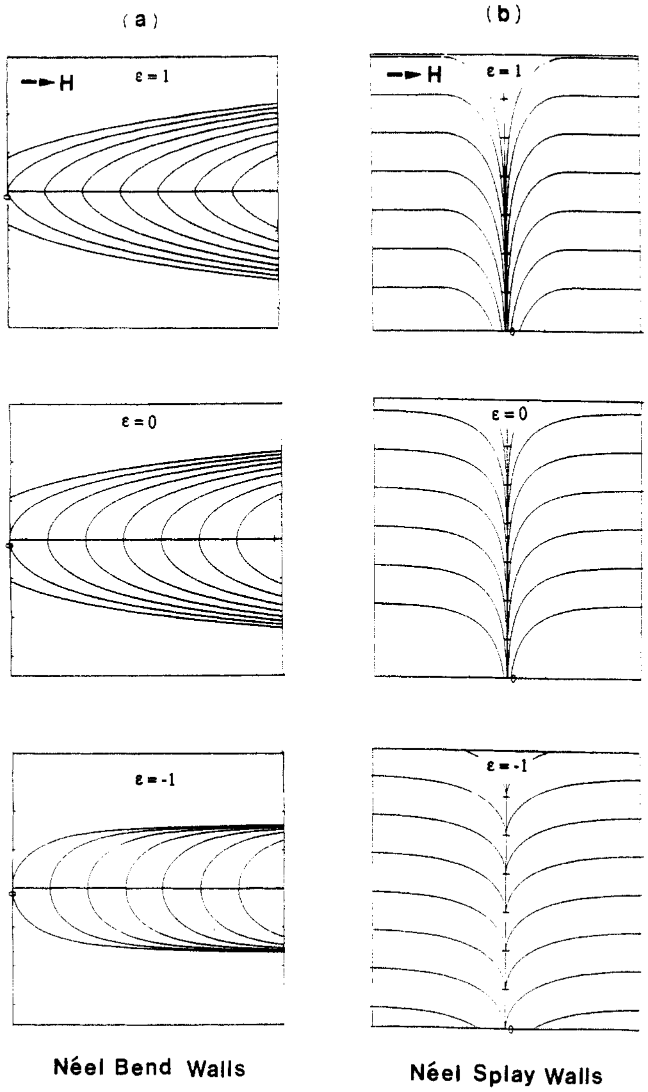


Figure 1. Schematics of the molecular director across π inversion walls: (a) Néel bend–splay walls parallel to the field at different values of elastic anisotropy and (b) Néel splay–bend walls normal to the field at different values of elastic anisotropy. These figures are based on the numerical solutions in Figure 2.

Néel Inversion Wall, $\epsilon \neq 0$. We introduce the elastic anisotropy, $\epsilon = (k_{11} - k_{33})/(k_{11} + k_{33})$, a new characteristic length $\zeta = (1/H)((k_{11} + k_{33})/\chi_a)^{0.5}$, and the dimensionless distance $x' = x/\zeta$, such that the differential equation of the Néel bend wall (more bend character in the bend–splay wall) can be rewritten as

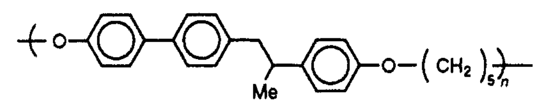
$$\sin\phi\cos\phi + \epsilon\sin\phi\cos\phi\left(\frac{d\phi}{dx'}\right)^2 + \left(\epsilon\sin^2\phi - \frac{1+\epsilon}{2}\right)\frac{d^2\phi}{dx'^2} = 0 \quad (2)$$

The differential equation (2) can be solved using the Runge–Kutta method for different values of the elastic anisotropy, ϵ. Since the director field across the wall should be symmetric, the director orientation only needs to be calculated from a sufficiently distant location x'_f, such that $\phi(x'_f) \approx 0$, up to the center of the inversion wall where $\phi(0) = \pi/2$. In practice, the differential equation is solved from $x' = -5$ (where the initial director orientation is guessed) to $x' = 0$. If $\phi(x'{=}0) \neq \pi/2$, a new initial value of the director orientation is chosen and the director orientation is calculated until the director angle is equal to $\pi/2$ at $x' = 0$ (within 0.05% error). Solutions of $\phi(x')$ are shown in Figure 2a. As expected, the solutions show that the director field across the inversion wall depends significantly on the elastic anisotropy. The change of the director orientation is almost constant for easy splay ($\epsilon = -1$) from the center of the inversion wall until $x' \approx 1.5$, whereas the change of the director is rather continuous until $x' \approx 2.5$ for the easy bend case ($\epsilon = 1$). The director trajectories of the Néel bend wall are plotted in Figure 2b. Because eq 2 cannot be solved for $\epsilon = -1$, we used the approximation $\epsilon = -0.99$ for the numerical calculation.

For the Néel splay wall, the differential equation of the inversion wall is identical to eq 1 except k_{11} and k_{33} are switched. Solutions of $\phi(x')$ are thus the same, except the elastic anisotropies are switched. That means the change of the director orientation is almost constant for easy bend from the center of the inversion wall until $x' \approx 1.5$, whereas the change of the director is rather continuous until $x' \approx 2.5$ for the easy splay case (see Figure 2a). The director trajectories of a Néel splay wall are precisely orthogonal to the director trajectories of a Néel bend wall, and the magnetic field direction is rotated by 90° with respect to the wall direction. It is evident from Figure 2b of a Néel bend wall that, for $\epsilon = -1$ (easy splay), the molecules align with the field more slowly than for the $\epsilon = +1$ (easy bend) case, whereas from Figure 2c, in a Néel splay wall, the opposite is true.

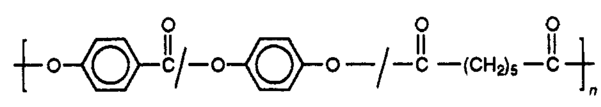
Experiment and Analysis

Inversion wall structures of two nematic main-chain thermotropic liquid crystalline polymers are analyzed. A semiflexible main-chain polyether (MEBB5) has been supplied by Percec:



The crystal to nematic transition temperature is 148 °C, and the nematic to isotropic transition occurs at 180 °C.

The specimen previously examined in Hudson et al.[2] was a random terpolymer of equal molar amounts of hydroxybenzoic acid, hydroquinone, and pimelic acid (HBA/HQ/PA):



Its number-average molecular weight is 3000; the crystal to nematic transition is 180 °C, and the nematic to isotropic transition is 250 °C.

A 1–2-μm thin film of each polymer was first sheared with a razor blade on a glass slide in the liquid crystalline state. In order to create inversion walls, the specimen was aligned in a 13.5-T magnetic field which was oriented in the plane of the specimen and perpendicular to the initial shearing direction. The sample was placed in the field for 30 min at 160 °C for the MEBB5 polymer and for 30 min at 230 °C for the HBA/HQ/PA polymer and then quenched to room temperature at a rate of ~10 °C/s with a flow of nitrogen gas. After appropriate annealing, the quenched glassy nematic polymer partially crystallizes into a lamellar morphology. The variations in the director field are easily rendered visible by the lamellae, which are perpendicular to the local director.[12]

A Néel splay inversion wall which is normal to the field appears as a Néel bend wall in the AFM (or SEM[2]) image due to the orthogonal relation between the long axis of the lamellae and the director. Conversely, a wall parallel to the field is a Néel bend wall, which appears as a splay wall in the image of the lamellae. A different curvature of the lamellae in the two types of Néel walls would directly indicate different values of elastic anisotropy as shown in Figure 1.

Detailed measurements of $\phi(x')$ were made as a function of distance from straight sections of π inversion walls oriented approximately parallel to and normal to the magnetic field. It is straightforward to qualitatively estimate the sign of ϵ, i.e., easy

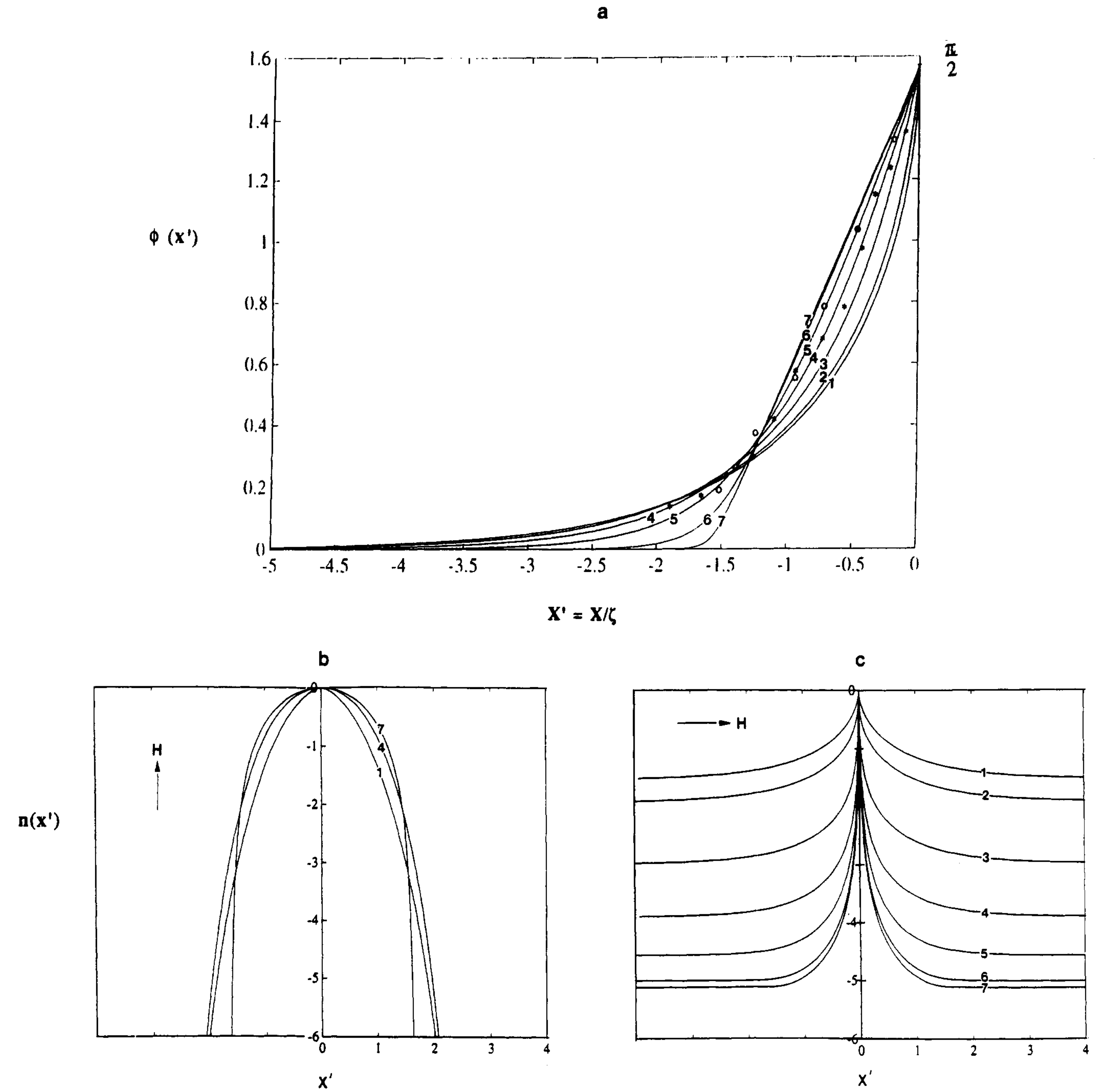


Figure 2. (a) Numerical solutions of director fields across Néel bend and Néel splay walls at different values of elastic anisotropy. Curves 1–7 are the solutions of ϵ = 1, 0.9, 0.5, 0, −0.5, −0.9, and −1 for Néel bend walls, while curves 1–7 correspond to ϵ = 1, −0.9, −0.5, 0, 0.5, 0.9, and 1, respectively, for Néel splay walls. Open circles and asterisks represent the measured values utilizing the lamellar decoration method for a AFM and HRSEM[2] image. The best fit of the experimental data for MEBB5 (open circles) is $\epsilon \approx 0.5$ and for HBA/HQ/PA (asterisk) is $\epsilon \approx 0$. (b) Calculated director orientation across Néel bend walls. (c) Calculated director orientation across Néel splay walls. Curve 1 is the molecular trace for the easy splay case in Néel splay walls. Curve 1 also represents the lamellar image of a Néel bend wall for the easy bend case.

bend or easy splay, from the curvature of the director with respect to position. The width of the inversion walls was fit by trial and error to determine the value of elastic anisotropy. Note the orthogonal relationship between molecular trajectories and lamellae and the reversed sign of elastic anisotropy of the Néel bend and Néel splay wall from the differential equation. For example, the curvature of the lamellae imaged of a portion of Néel splay wall of the MEBB5 polymer in Figure 3 appears to be similar to the director trajectories within the range of $-1 < \epsilon < 0$ in Figure 1a of the Néel bend wall. This means that for MEBB5 $k_{33} < k_{11}$. Open circles in Figure 2a show the values of the director orientation with respect to the dimensionless distance, $\phi(x')$. The measured elastic anisotropy is therefore approximately 0.5; i.e., $k_{11} = 3k_{33}$. The (new) characteristic length, ζ, was found to be 450 nm. Using a typical value of χ_a, which is on the order of 1.0×10^{-7} emu·cgs/g for semiflexible main-chain liquid crystal polymers,[16] and assuming a density of 1.0 g/cm^3 give approximate values of $k_{11} = 2.8 \times 10^{-6}$ dyn and $k_{33} = 0.9 \times 10^{-6}$ dyn, respectively. These values are typical of small-molecule and semiflexible polymer nematics.

THe $\phi(x')$ data from Hudson et al.[2] indicate the elastic anisotropy of HBA/HQ/PA is approximately zero (Figure 2a), which is quite compatible with the result from previous measurements on the director field distribution around a disclination in this polymer.[13] The estimated average elastic constant for HBA/HQ/PA was determined as 2.3×10^{-6} dyn.

Discussion

From our analysis, the width of both the Néel bend and Néel splay walls is expected to be the same in a given specimen since both the splay and bend elastic constants

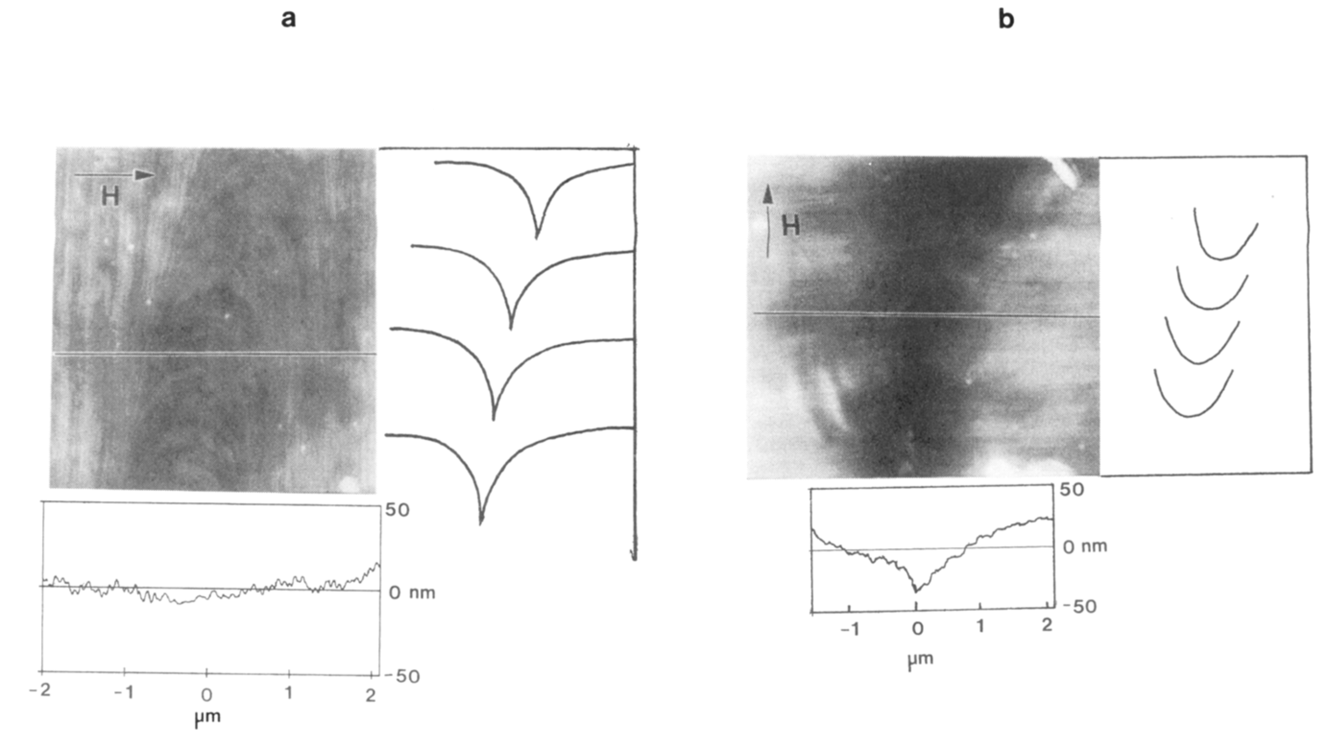


Figure 3. (a) AFM micrograph of a portion of the Néel splay inversion wall in MEBB5. The observed lamellae are perpendicular to the local molecular director, and the deformation is approximately two dimensional. (b) Height variation across the Néel bend inversion wall indicating a small amount of out-of-plane (twist) deformation.

enter into the characteristic width of the wall. Comparing the new characteristic length, which we call $\zeta = (1/H)((k_{11} + k_{33})/\chi_a)^{0.5}$, which combines both the splay and bend constants, with the characteristic length of the equal elastic constant case, $\xi = (1/H)(k_{11}/\chi_a)^{0.5}$ shows that $\zeta = 2^{1/2}\xi$ when the elastic constants are equal. Thus, the average elastic constant obtained from measurement of the characteristic length is the arithmetic average instead of a geometric average or some other average.

Although the Néel inversion (splay–bend) walls have been theoretically recognized by Helfrich, details on the molecular trajectory of the Néel inversion walls have been seldom reported[2–4] or distinguished, especially for the Néel splay wall. The Néel bend and Néel splay walls are quite distinct, and they are easily identified via AFM (Figure 3a,b) or SEM images for samples which exhibit lamellar decoration.

The AFM image in Figure 3a also shows the height profile of the upper (free) surface of the sample containing a portion of the Néel splay wall in a thin region of the MEBB5 sample. The width of the inversion wall is around 1.5 μm, and the maximum height variation across wall is 0.015 μm. It is evident that the deformation of the director across the inversion wall is approximately two dimensional.

Since the twist elastic constant is usually the smallest in liquid crystals, twist deformation of the molecules should be considered. The equilibrium shape of closed inversion twist wall loops created by Freedericks transition is predicted to be elliptical.[17] Figueiredo Neto et al.[8] have calculated that twist deformation would lower the Néel bend wall energy during the Freedericks transition. However, the three-dimensional solution for Helfrich inversion walls has not yet been solved. A greater difference (15 nm) in height is observed across a Néel bend wall in the thicker area of the MEBB5 specimen (see Figure 3b). This suggests that out-of-plane twist deformation may take place in thicker regions. Understanding such three-dimensional director patterns provides a new challenge for liquid crystal physics.

Summary

We numerically solved the differential equation for Néel inversion walls with elastic anisotropy in the thin film (2D) approximation and calculated the director orientation across both the Néel bend and Néel splay walls for different values of elastic anisotropy. The elastic anisotropy of liquid crystal polymers may be obtained directly from microscopic images (TEM, SEM, or AFM) of inversion walls by measuring the director orientation with the lamellar decoration technique.[2,4,12] Combined with the measurement of the wall width, which provides the information of the arithmetic average of the splay constant and bend constant, the absolute value of elastic constants, k_{11} and k_{33}, can be obtained with knowledge of the magnetic susceptibility anisotropy.

Acknowledgment. The authors thank Professor V. Percec for providing the MEBB5 polymer. This research was supported by AFOSR Grants 90-0150 and 91-0078.

References and Notes

(1) Helfrich, W. *Phys. Rev. Lett.* **1968**, *21*, 1518.
(2) Hudson, S. D.; Vezie, D. L.; Thomas, E. L. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 657.
(3) Hudson, S. D.; Thomas, E. L. *Phys. Rev. A* **1991**, *44*, 8128.
(4) Ford, J. R.; Bassett, D. C.; Mitchell, G. R.; Ryan, T. G. *Mol. Cryst. Liq. Cryst.* **1990**, *180B*, 233.
(5) Meyer, R. B. *Polymer Liquid Crystals*; Ciferri, A., Drigbaum, W. R., Meyer, R. B., Eds.; Academic Press: New York, 1982; p 133.
(6) Sun, Z.; Kléman, M. *Mol. Cryst. Liq. Cryst.* **1984**, *111*, 321.
(7) Léger, L. *Mol. Cryst. Liq. Cryst.* **1973**, *24*, 33.
(8) Figueiredo Neto, A. M.; Martinot-Lagarde, P.; Durand, D. *J. Phys., Lett.* **1984**, *45*, L-793.
(9) Kléman, M. *Points, Lines, and Walls*; Wiley: Chichester, U.K., 1983.
(10) Mineev, V. P.; Volovik, G. E. *Phys. Rev.* **1978**, *B13*, 3197.
(11) Frank, F. C. *Discuss. Faraday Soc.* **1958**, *25*, 19.
(12) Thomas, E. L.; Wood, B. A. *Faraday Discuss. Chem. Soc.* **1985**, *79*, 229.
(13) Hudson, S. D.; Thomas, E. L. *Phys. Rev. Lett.* **1989**, *62*, 1993.

(14) Either a magnetic field or an elongational flow field. The differential equation governing for the director field under magnetic and flow fields is[15] $0 = [(\alpha_3 - \alpha_2)\,\partial/\partial t - k(\partial^2/\partial x^2 + \partial^2/\partial y^2)]\phi + \chi_a H^2 \sin(\phi-\phi_H)\cos(\phi-\phi_H) - 2(\alpha_3 + \alpha_2)\dot{e} \sin\phi \cos\phi - 2\dot{\gamma}(\alpha_3 \cos^2\phi - \alpha_2 \sin^2\phi)$. The effect of elongational flow on the director fields is expected to be analogous to that of an applied magnetic field. Hudson and Thomas[2] exploited this correspondence to observe texturing of defects in a nematic liquid crystal polymer. They found many inversion walls and characteristic disclination clusters in both types of fields.
(15) Stephen, M. J.; Straley, J. P. *Rev. Mod. Phys.* **1974**, *46*, 617.
(16) Hardouin, F.; Achard, M. F.; Gasparoux, H.; Liebert, L.; Strzelecki, L. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 975.
(17) Brochard, F. *J. Phys. (Paris)* **1972**, *33*, 607.