

# Role of electrostatics in the texture of islands in free-standing ferroelectric liquid crystal films

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Curved textures of ferroelectric smectic- $C^*$  liquid crystals produce space charge when they involve divergence of the spontaneous polarization field. Impurity ions can partially screen this space charge, reducing long-range interactions to local ones. Through studies of the textures of islands on very thin free-standing smectic films, we see evidence of this effect, in which materials with a large spontaneous polarization have static structures described by a large effective bend elastic constant. To address this issue, we calculated the electrostatic free energy of a free-standing film of ferroelectric liquid crystal, showing how the screened Coulomb interaction contributes a term to the effective bend elastic constant, in the static long-wavelength limit. We report experiments which support the main features of this model.

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The inclusion of submicrometer particles in a very thin free-standing ferroelectric smectic- $C^*$  ( $Sm-C^*$ ) film induces the growth of islands, circular regions of thicker material, usually with a central point topological defect surrounded by a texture which satisfies certain boundary conditions and minimizes an appropriate free energy [1,2]. In the simplest case, this is a pure bend texture, with the molecules oriented tangentially everywhere in the island and the topological defect, or disclination, at the center. This yields a radial spontaneous polarization  $\mathbf{P} = \pm P_0 \hat{r}$  whose divergence produces space charge [3]. Thus the electrostatic interaction in this pure bend island should play an important role in the energetics of the liquid crystal texture. In our initial studies [2], we performed a purely elastic analysis of the free energy of the observed textures and found that our observations of textural transitions as a function of island diameter were well explained by a large ratio of bend to splay elastic constants. We observed that this large ratio correlated with a large spontaneous polarization in the material studied. This suggested that the observed large effective bend elastic constant actually arose from the electrostatic interaction. In this paper, we report experiments and theory which develop the evidence for this scenario, which explains well our observations.

The long-range electrostatic interaction arising from divergence of the spontaneous polarization field has been studied previously, as has the screening of that interaction by dissolved impurity ions in the liquid crystal [4]. In  $Sm-C^*$  free-standing films, the impurity ion effect first was observed qualitatively by Pindak *et al.* [5]. Subsequently, the screening effect by impurity ions in  $Sm-C^*$  free-standing films was studied experimentally in Refs. [6,7]. Theoretically Okano showed that in the long-wavelength limit in a bulk ferroelectric liquid crystal, the screened Coulomb interaction reduced to an effective bend elastic constant, whose magnitude depends on the concentration of impurity ions and the size of the spontaneous polarization [8]. This analysis followed that of Palierne, who discussed the ionic screening of the electric

field produced by flexoelectric polarization in the nematic phase in three dimensions [9]. For a thin film, the geometry of screening effects is different, since the sources of the electric field and the screening ions are confined to two dimensions, while the field propagates in three dimensions. Nevertheless, we thought that such ionic screening of the space charge arising from spontaneous polarization might change the long-range electrostatic energy into a local effective elastic term even in the case of thin films.

A textural transformation which we have studied in the islands is from a pure bend (tangential) pattern to a reversing spiral texture [2,10,11]. In the reversing spiral texture, shown in Fig. 1(a) the tangential boundary conditions of the  $c$  director (a unit vector parallel to the projection of the tilted molecular orientation direction on the plane of the film) still apply at both the outer boundary and the point defect at the center, but the  $c$  director switches to a radial orientation between these two limits. This partially replaces bend with splay deformation, reducing the elastic energy if the splay elastic constant is less than the bend elastic constant. As islands grow, this transition occurs at a critical island size, which is then a measure of the relative magnitudes of these two elastic constants. We investigated the textures of islands in commercial ferroelectric liquid crystal mixtures, which have a  $Sm-C^*$  phase at room temperature. The ferroelectric liquid crystal mixtures we used are the CS series (CS1015, CS1024, CS2005) by Chisso and the RO series (RO318, RO322, RO330) by RODIC. Based on the company specifications, measured at room temperature, CS1024 and CS2005 have relatively high spontaneous polarization (46.7 nC/cm<sup>2</sup> and 72.6 nC/cm<sup>2</sup>, respectively) and CS1015, RO318, RO322, and RO330 have very low spontaneous polarization (6.6 nC/cm<sup>2</sup>, 3 nC/cm<sup>2</sup>, 3.8 nC/cm<sup>2</sup>, and 3.8 nC/cm<sup>2</sup>, respectively).

Islands commonly created in CS1024 and CS1015 are shown in Figs. 1(a) and 1(b). In islands on the film with a high spontaneous polarization, the pure bend texture is rarely seen. Most of them show a reversing spiral texture or a boojum texture [Fig. 1(a)]. On the other hand, as shown in Fig. 1(b), all of the islands are pure bend islands or boojum islands at equilibrium; RO318, RO322, and RO330 show very

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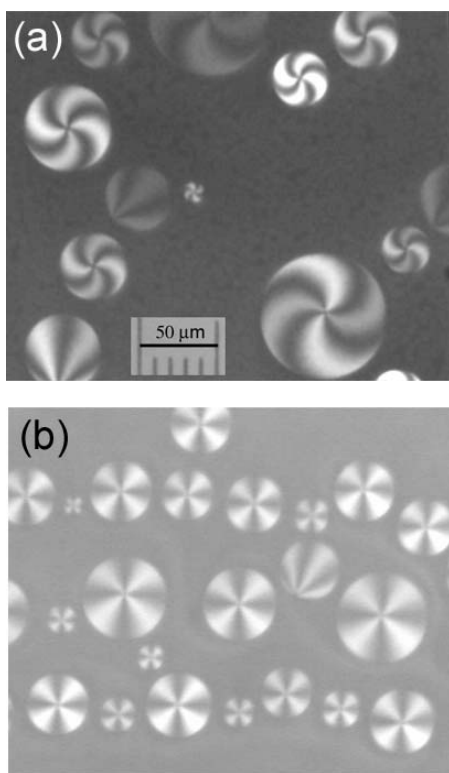


FIG. 1. Textures of islands viewed between crossed polarizers. (a) Islands shown in CS1024, typical of a high-spontaneous-polarization material ( $46.7 \text{ nC/cm}^2$ ). (b) Islands seen in CS1015, a low-spontaneous-polarization material ( $6.6 \text{ nC/cm}^2$ ).

similar textures, in which a reversing spiral island is observed only at an unusually large island size. We also never observed pure bend islands in a ferroelectric liquid crystal compound with an extremely high spontaneous polarization [12]. Hence the reversing spiral texture, which is an indicator of a large ratio of bend to splay elastic constants, is directly correlated with a large spontaneous polarization.

To observe the spontaneous polarization dependence of the textural transition from a pure bend into a reversing spiral, we investigated the textures of islands created in mixtures of two ferroelectric liquid crystals with high and low spontaneous polarizations. The critical size for a pure bend island to start to change into a reversing spiral was measured as the ratio of the two materials was varied, as shown in Fig. 2, where data on mixtures of CS1024 and CS1015 and CS2005 and RO318 are shown. The real-time transformation is shown in Ref. [2]. The islands marked by the arrow are just initiating the transformation to the reversing spiral texture. Larger islands than the marked ones have already transformed into the reversing spiral texture, but smaller islands are still in the pure bend texture. A higher proportion of the material with high spontaneous polarization causes a pure bend island to transform into a reversing spiral texture at a smaller critical radius. Other mixtures of high- and low-spontaneous-polarization materials show very similar behavior.

In order to relate our study of the quasistatic textural transformation to fundamental liquid crystal properties, we undertook measurements of fundamental liquid crystal prop-

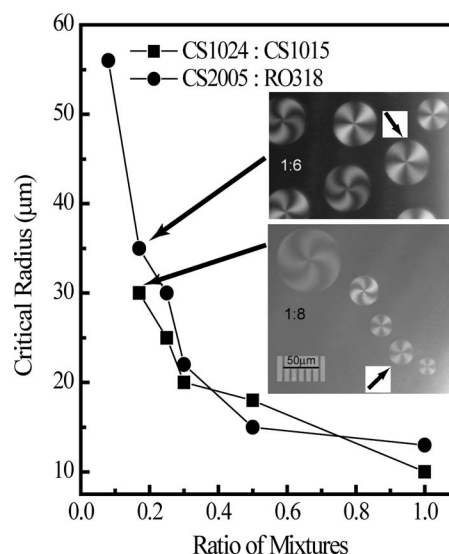


FIG. 2. Critical radius for transition from pure bend to reversing spiral vs weight ratio of a high-spontaneous-polarization to a lower-spontaneous-polarization material. The islands marked by arrows are just above the critical radius. Top: a mixture of CS1024 and CS1015 with a 1:8 mass ratio. Bottom: a mixture of CS2005 and RO318 with a 1:6 mass ratio.

erties of the mixtures in which we made textural observations. Knowing that the screening of the space charges by mobile ions is a slow process, we undertook measurements of the elastic properties of these thin films in fast dynamic processes, to obtain values of “bare” elastic constants, as well as spontaneous polarizations. We measured the elastic constants and spontaneous polarizations of the free-standing films (four smectic layers thick) created by CS1024, CS1015, and their mixtures by monitoring the change of intensity of light scattered by  $c$ -director fluctuations due to quenching of the fluctuations by a strong electric field pulse, following the work of Rosenblatt *et al.* [13]. The results are listed in Table I. As we expected, a larger proportion of the higher-spontaneous-polarization material increases the spontaneous polarization of the mixture. However, the bare splay elastic constants measured with fast dynamics were found to be larger than the bend elastic constants in the mixtures. This should favor the pure bend texture, in disagreement with our observations in the quasistatic limit, which indicated that the bend elastic constant is larger. This supported our guess that

TABLE I. Spontaneous polarization and elastic constants determined by the electric field quenching experiment.

Materials	$P_0$ ( $10^{-5}$ esu/cm)	$K_b$ ( $10^{-12}$ erg)	$K_s$ ( $10^{-12}$ erg)
CS1024	7.97	4.27	2.43
1:2 <sup>a</sup>	5.49	3.12	3.62
1:3	5.27	2.09	2.83
1:5	2.55	0.89	1.12
1:8	2.45	0.71	1.45
CS1015	2.45	0.39	2.64

<sup>a</sup>Ratio of CS1024 to CS1015.

the screened electrostatic interactions were contributing to the apparently large quasistatic bend elastic constant.

To address this issue theoretically, we calculate the electrostatic free energy of a very thin film. We assume that the liquid crystal film lies in the plane  $z=0$ , surrounded by vacuum on both sides. Mathematically we treat the film as infinitesimally thin, but introduce the film thickness  $a$  in an appropriate dimensional fashion. Denoting the dielectric constant of the film (assumed to be spatially uniform) by  $\epsilon$ , the dielectric function for the three-dimensional space is given by

$$\epsilon'(z) = 1 + (\epsilon - 1)a\delta(z). \quad (1)$$

Gauss' law then reads

$$\nabla \cdot [\epsilon'(z)\mathbf{E}(\mathbf{r})] = 4\pi\rho(\mathbf{r}), \quad (2)$$

where  $\rho(\mathbf{r}) = \rho_{ion}(\mathbf{r}) + \rho_P(\mathbf{r})$  is the sum of the ionic and ferroelectric space-charge densities, respectively. These densities are proportional to  $\delta(z)$ . Note that  $\mathbf{r} = (\mathbf{r}_\perp, z)$  and  $\nabla = (\nabla_\perp, \partial/\partial z)$  are three-dimensional vectors.

Using Eq. (1), Gauss' law can be rewritten as

$$\begin{aligned} \nabla \cdot [\epsilon'(z)\mathbf{E}] &= \nabla \cdot \{[1 + (\epsilon - 1)a\delta(z)]\mathbf{E}\} \\ &= [1 + (\epsilon - 1)a\delta(z)]\nabla \cdot \mathbf{E} \\ &\quad + (\epsilon - 1)aE_z\delta'(z), \end{aligned} \quad (3)$$

where  $\delta'(z) \equiv d\delta(z)/dz$ . Introducing the electrostatic scalar potential  $\Phi(\mathbf{r})$  defined as usual by  $\mathbf{E} = -\nabla\Phi$  we obtain a Poisson-like equation from Eq. (3),

$$-[1 + (\epsilon - 1)a\delta(z)]\nabla^2\Phi(\mathbf{r}) - (\epsilon - 1)a\delta'(z)\frac{\partial\Phi(\mathbf{r})}{\partial z} = 4\pi\rho(\mathbf{r}). \quad (4)$$

We now treat the ionic charge density using the Debye-Hückel approximation. Assuming that there are  $n$  species of ionic impurities and that the average concentration of the  $i$ th type of impurity is  $c_i$ , the local concentration  $c_i(\mathbf{r})$  of this impurity at position  $\mathbf{r}$  is given by the Boltzmann distribution:

$$c_i(\mathbf{r}) = c_i \exp[-\beta e_i\Phi(\mathbf{r})]\delta(z), \quad (5)$$

where  $e_i$  is the charge of the impurity of type  $i$  and  $\beta \equiv 1/k_B T$ . The total ionic charge density at position  $\mathbf{r}$  is then given by

$$\rho_{ion}(\mathbf{r}) = \sum_{i=1}^n e_i c_i \exp[-\beta e_i\Phi(\mathbf{r})]\delta(z). \quad (6)$$

We insert this charge density into Eq. (4) and linearize in  $\Phi$  to obtain a Debye-Hückel equation

$$\begin{aligned} &-[1 + (\epsilon - 1)a\delta(z)]\nabla^2\Phi(\mathbf{r}) - (\epsilon - 1)a\delta'(z)\frac{\partial\Phi(\mathbf{r})}{\partial z} \\ &+ 4\pi\beta \sum_{i=1}^n e_i^2 c_i \Phi(\mathbf{r})\delta(z) = 4\pi\rho_P(\mathbf{r}). \end{aligned} \quad (7)$$

Replacing the space charge  $\rho_P$  by a  $\delta$ -function source, we obtain the equation obeyed by the Green's function  $G(\mathbf{r})$  associated with Eq. (7):

$$\begin{aligned} &-[1 + (\epsilon - 1)a\delta(z)]\nabla^2 G(\mathbf{r}) - (\epsilon - 1)a\delta'(z)\frac{\partial G(\mathbf{r})}{\partial z} \\ &+ \kappa G(\mathbf{r})\delta(z) = 4\pi\delta(\mathbf{r}), \end{aligned} \quad (8)$$

where the inverse two-dimensional (2D) Debye screening length  $\kappa$  is given by

$$\kappa = 4\pi\beta \sum_{i=1}^n e_i^2 c_i. \quad (9)$$

Fourier transforming Eq. (8) we obtain

$$q^2 G(\mathbf{q}) + \int \frac{dq'_z}{2\pi} G(\mathbf{q}_\perp, q'_z) [(\epsilon - 1)aq_\perp^2 + \kappa] = 4\pi, \quad (10)$$

where  $\mathbf{q}_\perp$  is the projection of  $\mathbf{q}$  in the plane of the film and we have used the fact that  $G$  is an even function of  $q_z$ . From Eq. (10) we find

$$G(\mathbf{q}) = \frac{4\pi - [(\epsilon - 1)aq_\perp^2 + \kappa] \int \frac{dq'_z}{2\pi} G(\mathbf{q}_\perp, q'_z)}{q_z^2 + q_\perp^2}. \quad (11)$$

Integrating both sides of this equation over  $q_z$  we obtain

$$\int G(\mathbf{q}_\perp, q_z) dq_z = \frac{4\pi^2}{q_\perp + \frac{(\epsilon - 1)aq_\perp^2}{2} + \frac{\kappa}{2}}, \quad (12)$$

which we will now use to obtain an expression for the screened electrostatic energy.

The electrostatic energy  $F_{elec}$  of the film is given by

$$F_{elec} = \frac{1}{2} \int \rho_P(\mathbf{r}_\perp)\Phi(\mathbf{r})d^3\mathbf{r}, \quad (13)$$

where the space charge  $\rho_P(\mathbf{r}_\perp) = -\nabla \cdot \mathbf{P}$ . In terms of the Green's function  $G(\mathbf{r})$ ,  $F_{elec}$  can be expressed as

$$F_{elec} = \frac{1}{2} \int \int d^3r d^3r' \rho_P(\mathbf{r}_\perp)\rho_P(\mathbf{r}'_\perp)\delta(z)\delta(z')G(\mathbf{r} - \mathbf{r}'), \quad (14)$$

which in Fourier space yields

$$F_{elec} = \frac{1}{2} \int \frac{d^2q_\perp}{(2\pi)^2} \rho_P(\mathbf{q}_\perp)\rho_P(-\mathbf{q}_\perp) \int \frac{dq_z}{2\pi} G(\mathbf{q}_\perp, q_z). \quad (15)$$

Using Eq. (12) we obtain

$$F_{elec} = \frac{1}{2} \int \frac{d^2q_\perp}{(2\pi)^2} \rho_P(\mathbf{q}_\perp)\rho_P(-\mathbf{q}_\perp) \frac{2\pi}{q_\perp + \frac{(\epsilon - 1)aq_\perp^2}{2} + \frac{\kappa}{2}}. \quad (16)$$

In the long-wavelength limit, where  $q_\perp$  is much smaller than the inverse 2D screening length  $\kappa$ ,  $F_{elec}$  simplifies to

$$F_{elec} = \frac{2\pi}{\kappa} \int \frac{d^2q_{\perp}}{(2\pi)^2} \rho_P(\mathbf{q}_{\perp}) \rho_P(-\mathbf{q}_{\perp}) \quad (17)$$

$$= \frac{1}{2} \int \frac{4\pi}{\kappa} (\nabla \cdot \mathbf{P})^2 d\mathbf{r}_{\perp}. \quad (18)$$

The polarization vector is given by  $\mathbf{P} = P_0 \hat{\mathbf{z}} \times \hat{\mathbf{c}}$ , where  $P_0$  is the magnitude of a spontaneous polarization. Using this expression in Eq. (18) we find

$$F_{elec} = \frac{1}{2} \int 4\pi\lambda_{2D} P_0^2 (\hat{\mathbf{z}} \cdot \nabla \times \mathbf{c})^2 d\mathbf{r}_{\perp}, \quad (19)$$

where  $\lambda_{2D} \equiv 1/\kappa$  is the 2D Debye screening length.

Hence, the total free energy of the film including the Frank elastic energy is

$$F = \frac{1}{2} \int [K_s (\nabla \cdot \hat{\mathbf{c}})^2 + (K_b + 4\pi\lambda_{2D} P_0^2) (\hat{\mathbf{z}} \cdot \nabla \times \hat{\mathbf{c}})^2] d\mathbf{r}_{\perp}, \quad (20)$$

where  $K_s$  and  $K_b$  are the splay and bend elastic constants, respectively. Thus the screening by the impurity ions has rendered the elastic free-energy density local. Therefore, an effective bend elastic constant can be defined:

$$K_b^{eff} = K_b + 4\pi\lambda_{2D} P_0^2, \quad (21)$$

similar to the result obtained for bulk ferroelectric liquid crystals [8].

We have shown that the electrostatic energy due to space charge created by divergence of the spontaneous polarization, screened by impurity ions dissolved in the liquid crystal, can become a local effective term in the elastic free energy in the case  $q \ll 1/\lambda_{2D}$ . This means that a term  $\lambda_{2D} P_0^2$  can dominate the bare bend elastic constant  $K_b$  in that limit. This is reflected in the change of the critical size for the transition from a pure bend island to a reversing spiral, when varying the spontaneous polarization or the concentration of the impurity ions, which tunes  $\lambda_{2D}$ . The combination of large spontaneous polarization and low concentration of screening ions produces the largest increase in the effective bend elastic constant.

In order to see the effect of the impurity ions, we added free ions to the material to reduce the 2D Debye screening length as shown in Eq. (9). We doped our ferroelectric liquid crystal mixtures with an organic salt, tetrabutylammonium bromide (TBAB) (99+% purity by Acros Organic), at saturated concentration in a mixture of RO318 and CS2005 with a composition ratio of 1:5. Before the salt was added, reversing spiral islands existed at a small size [Fig. 3(a)]. As shown in the top of Fig. 3(b), most islands on the film doped with TBAB are in the pure bend texture. Reversing spiral islands only appear at a larger critical size than seen in Fig. 3(a). Although this result is qualitative, it indicates the trend of the effect. It would be desirable to find an appropriate salt with greater solubility and to make quantitative measurements of ionic concentration for this experiment.

In summary, we studied the textural transformation from a

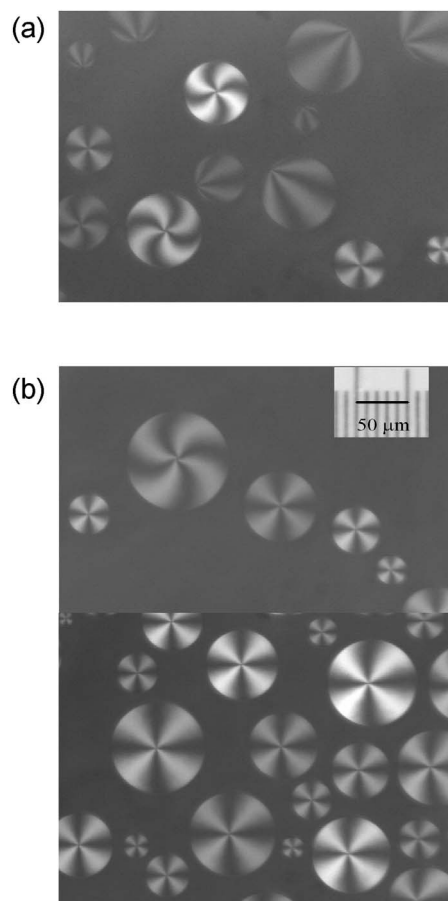


FIG. 3. Effect of impurity ions. (a) These islands are observed on a film composed of RO318 and CS2005 with a 1:5 composition ratio. (b) After doping with an organic salt, most islands are in the pure bend texture. The critical radius for the transition to the reversing spiral texture has increased due to the smaller effective bend elastic constant.

pure bend island to a reversing spiral texture in islands on thin films of smectic- $C^*$  ferroelectric liquid crystals. We observed that the transition size of the islands depends on the spontaneous polarization of the material. Based on this observation, we proposed that the spontaneous polarization and Debye screening length regulate the effective bend elastic constant in the long-wavelength limit. The typical Debye screening length in these materials has subsequently been measured to be about  $0.7 \mu\text{m}$  [14], in separate experiments to be reported elsewhere. Our typical island size is tens of micrometers, so the conditions for use of this effective bend elastic constant to describe the electrostatic energy appear to be reasonable. As a qualitative test of this model, we observed that added impurity ions reduced the effective bend elastic constant.

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- [1] R. B. Meyer, D. Konovalov, I. Kraus, and J.-B. Lee, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **364**, 123 (2001).
- [2] J.-B. Lee, D. Konovalov, and R. B. Meyer, *Phys. Rev. E* **73**, 051705 (2006).
- [3] R. B. Meyer, L. Liebert, and P. Keller, *J. Phys. (France) Lett.* **36**, L69 (1975).
- [4] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, 2nd ed. (Clarendon Press, Oxford, 1995).
- [5] R. Pindak, C. Y. Young, R. B. Meyer, and N. A. Clark, *Phys. Rev. Lett.* **45**, 1193 (1980).
- [6] J. MacLennan, *Europhys. Lett.* **13**, 435 (1990).
- [7] R. Holyst, A. Poniewierski, P. Fortmeier, and H. Stegemeyer, *Phys. Rev. Lett.* **81**, 5848 (2000).
- [8] K. Okano, *Jpn. J. Appl. Phys., Part 2* **25**, L846 (1986).
- [9] J. F. Palierne, *Phys. Rev. Lett.* **56**, 1160 (1986).
- [10] I. Kraus and R. B. Meyer, *Phys. Rev. Lett.* **82**, 3815 (1999).
- [11] K. K. Loh, I. Kraus, and R. B. Meyer, *Phys. Rev. E* **62**, 5115 (2000).
- [12] The ferroelectric liquid crystal compound is mesogenic silane W399, whose spontaneous polarization is  $425 \text{ nC/cm}^2$  at  $25^\circ\text{C}$ . We thank David Walba (University of Colorado) for the gift of the material.
- [13] C. Rosenblatt, R. Pindak, N. A. Clark, and R. B. Meyer, *Phys. Rev. Lett.* **42**, 1220 (1979).
- [14] J.-B. Lee, Ph.D. thesis, Brandeis University, 2004.