Elasticity of rubber with smectic microstructure

M. J. Osborne and E. M. Terentjev

Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, United Kingdom

(Received 7 April 2000)

Using a physically motivated continuum model for the free energy of an elastomer with a smectic or lamellar microstructure, we examine the effects of coupling between the smectic and the rubber-elastic degrees of freedom on measurements of the layer structure and elastic moduli. In agreement with experiment, we find that the elastic response to stretching along the layer normal is greatly increased by the smectic layering, while the modulus parallel to the layers is unchanged. We show that Landau-Peierls instability of fluctuations in the layer structure of ordinary smectic liquid crystals is removed by the elastic matrix. Consequently one sees Bragg peaks in the diffraction pattern of a solid with one-dimensional order and we calculate the Debye-Waller factors for these.

PACS number(s): 61.30.Cz, 61.41.+e, 83.20.Bg

I. INTRODUCTION

Liquid-crystal elastomers are materials displaying both liquid-crystalline order and a sparse crosslinked network of flexible polymers. There are thus two types of degrees of freedom in elastomer liquid crystals, those associated with liquid-crystalline order and those associated with the rubber-elastic matrix. These two degrees of freedom are coupled together and it is the interplay between them that gives the liquid-crystal elastomers their unusual mechanical characteristics. One of the most startling is the effect of soft deformation in the case of nematic rubbers [1]. Here, for certain modes of deformation, realignment of the director produces an exactly equivalent molecular arrangement after deformation. Consequently, in the ideal case there is no energy penalty for such deformations [2].

In this paper we examine another case of rubbery elastic material with microstructure: lamellar or smectic elastomers. Smectic elastomers and gels, or permanently crosslinked networks of polymer chains that spontaneously form smectic or lamellar phases, are just as frequent as the nematic ones. From the symmetry point of view there is a great variety of possible phases, combining the one-dimensional (1D) smectic order with various degrees of positioning and alignment of mesogenic groups. We shall consider the most simple smectic order, called ''smectic-A'' or lamellar L_α phase, where the average molecular anisotropy axis is coaxial with the layer normal. In other words, the nematic director n (the principal axis of uniaxial optical birefringence) is locked perpendicular to the smectic layers. In many molecular systems the smectic-A or L_α-lamellar order is all the material can achieve in terms of intermediate degree of order between a fully isotropic and a crystalline or glassy state. Examples of such systems, one way or another, involve polymer chains that are prone to microphase separation: block copolymers [3,4] or polysurfactants [5]. Independently, a substantial effort has been put, over the years, into synthesizing and crosslinking the naturally liquid-crystalline polymers possessing smectic phases.

Figure 1 shows a schematic smectic-A alignment of side-chain liquid-crystalline polymers. In fact, since their first appearance in the early 1980's (e.g., Refs. [6] and [7]), such

polymers are more frequently found smectic than nematic. The reason for this is straightforward: a tendency for microphase separation between aligned rodlike mesogenic groups and the polymer backbone results in the layered morphology.

A crosslinking strategy in preparing smectic networks has to take into account certain molecular constraints. In fact, the sketch in Fig. 1(c) illustrates that one needs to be careful in selecting the size of crosslinking molecular groups. From the geometric point of view they have to have a length equal to an integer of the smectic layer spacing d_0. A pointlike crosslink would bind backbones confined within one interlayer plane. The same applies to a flexible chain binding two backbones—this, in some sense, accounts for two pointlike crosslinks. A rodlike crosslink such as bi-functional groups shown in Fig. 1(c) would bind backbones across a layer, if its length is $\approx d_0$. Anything in between would create a strong distortion of the local smectic order near an incommensurate crosslink [8] and, therefore, would depress the existence of the phase. The crosslinking of polymers in the smectic phase creates a local dependence between the crosslink and the layer position and their relative movement along the layer normal should be difficult. We shall soon return to this point, crucial to the understanding of smectic rubber elasticity. Note that the position of crosslinks has no effect in the homogeneous nematic phase: one needs to break the transla-
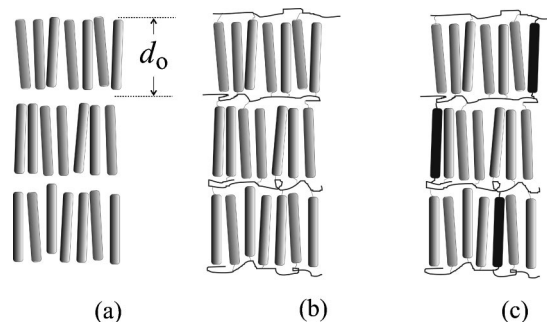

FIG. 1. Schematic drawing of mesogenic group arrangement in smectic-A phase of (a) liquid-crystal, (b) side-chain polymer with the backbone confined between the layers, and (c) elastomer with crosslinking groups (darkened) incorporated into the smectic layers.

tional symmetry of mesophase in order to experience such a coupling.

As with nematic networks, the conditions of crosslinking define the texture of the resulting mesophase. When the network is formed in the isotropic phase or when no special aligning procedure is applied, the liquid-crystalline elastomer invariably forms a polydomain texture of very small characteristic size. Polydomain nematic and smectic elastomers and gels strongly scatter light and, thus, appear opaque. In contrast, when the final crosslinking of the network is performed in an aligned state (whether in a mesophase or in the isotropic state, for instance, by applying a stress or a strong magnetic field, which is then frozen in by crosslinking) the monodomain liquid-crystalline phase results. In this way, by uniaxially stretching the material before final crosslinking, Nishikawa and Finkelmann [9] have produced the required symmetry breaking with a principal axis determining the layer normal in resulting monodomain smectic-A elastomers. The subsequent heating into the isotropic phase and cooling back into the smectic preserves this uniaxial alignment imposed by the stretching, with layers spontaneously forming in the plane perpendicular to the stress axis.

In this paper we develop a universal continuum description of monodomain nematic and smectic-A elastomers, examining the couplings between the director, the layer conformation, and the underlying rubber deformations. In the proposed theory, the smectic order parameter $|\psi|$ is allowed to change between zero (giving the correct limit of nematic rubber) and one (describing a strong smectic order). We calculate the effect of smectic order on the effective elastic moduli and compare the results with the experimental data of Nishikawa and Finkelmann. We also reexamine the effect of layer fluctuations [10] and give an improved description of the Bragg scattering of smectic layers, with Debye-Waller factors determined by the crosslinking density and smectic order parameter.

II. THE CONTINUUM MODEL

In order to understand the physical properties of smectic elastomer networks, we need to examine the relevant variables describing different aspects of their behavior. We shall always compare these with the case of nematic elastomers, where there is a better theoretical understanding and much experimental data. In some materials this comparison has a direct benefit because they actually possess a nematic phase at a higher temperature, which then transforms into the smectic on cooling below the critical point T_{NA}. In many other cases there is no preceding nematic phase: some liquid crystals transform directly from isotropic into the smectic-A phase; the lamellar phase L_α is often the first stage of symmetry breaking from the isotropic homogeneous mixture or polymer blend. However, the final state of smectic elastomer should have macroscopic properties qualitatively the same, regardless of how this phase has been reached. Therefore, the results and conclusions we shall obtain by examining elastomers with nematic order and the added effect of layers, will be equally applicable to all lamellar systems once the nematic degrees of freedom are integrated out.

We, therefore, write the continuum free energy as the sum of the contributions for the ordinary nematic, the ordinary

smectic, and the elastomer; these are the three relevant degrees of freedom. These degrees of freedom couple with each other so that we have, in principle, three couplings between pairs of these to include in the free energy. Let us describe each of the contributions to the free energy in turn, starting from the small deformation limit of anisotropic elastic rubber.

A. Linear elasticity of nematic rubbers

As a first step in any continuum elastic theory, one identifies the translational degree of freedom, the vector of local displacement in the elastic network $V(r)$, with the coordinate r measured in the undistorted body. Here and below one should take care distinguishing this upper-case notation from the more traditional $v(r)$. We shall see later that in a phase where a microstructure has a broken translational symmetry even the constant absolute value of local displacement, e.g., a component V_z along the layer normal in the case of smectic-A, will contribute to a coupling free energy. In contrast, in a standard elasticity one only finds a role for relative translations expressed by the nonuniform part of the displacement vector $v(r)$. For instance, this describes the change in the end-to-end distance of a network strand $\mathbf{R} = \mathbf{R}_0 + v$. The gradients define the small deformation tensor $\mathsf{v}_{\alpha\beta} = \partial v_\alpha / \partial x_\beta$, the full affine Cauchy strain tensor being then $\lambda_{\alpha\beta} = \delta_{\alpha\beta} + \mathsf{v}_{\alpha\beta}$. Only the symmetric part $\varepsilon_{\alpha\beta} = \frac{1}{2}(\mathsf{v}_{\alpha\beta} + \mathsf{v}_{\beta\alpha})$ contributes to the ordinary elastic response. In a frame-independent form, the free-energy density of a uniaxial material is given by

$$F_{el} = C_1 (n \cdot \widetilde{\underline{\underline{\varepsilon}}} \cdot n)^2 + 2 C_2 \, \mathrm{Tr}[\underline{\underline{\varepsilon}}](n \cdot \widetilde{\underline{\underline{\varepsilon}}} \cdot n) + C_3 (\mathrm{Tr}[\underline{\underline{\varepsilon}}])^2$$
$$+ 2 C_4 [n \times \widetilde{\underline{\underline{\varepsilon}}} \times n]^2 + 4 C_5 ([n \times \widetilde{\underline{\underline{\varepsilon}}} \cdot n])^2, \quad (1)$$

with n the local axis of anisotropy (the undistorted nematic director or the smectic layer normal) and $\widetilde{\varepsilon}_{\alpha\beta} = \varepsilon_{\alpha\beta} - \frac{1}{3} \mathrm{Tr}[\underline{\underline{\varepsilon}}] \delta_{\alpha\beta}$ the traceless part of strain. In the given form, Eq. (1) is a standard expression for a uniaxial elastic material [12] and has exactly the same form as the one used in the linear theory of nematic elastomers [2], which is a result of the same point symmetry of the two phases. When the direction of n is chosen along the z axis, the elastic energy density takes a more familiar uniaxial form

$$F_{el} = C_1 \widetilde{\varepsilon}_{zz}^2 + 2 C_2 \widetilde{\varepsilon}_{zz} \mathrm{Tr}[\underline{\underline{\varepsilon}}] + C_3 (\mathrm{Tr}[\underline{\underline{\varepsilon}}])^2$$
$$+ 2 C_4 (\widetilde{\varepsilon}_{xx}^2 + 2 \widetilde{\varepsilon}_{xy}^2 + \widetilde{\varepsilon}_{yy}^2) + 4 C_5 (\widetilde{\varepsilon}_{xz}^2 + \widetilde{\varepsilon}_{yz}^2). \quad (2)$$

One expects that in a rubber or dense polymer melt the bulk modulus C_3 is very large, $C_3 \sim 10^9 - 10^{10}$ J/m^3. The three moduli C_1, C_4, and C_5 are of the same order of magnitude given by a typical rubber shear modulus $\mu \sim 10^4 - 10^6$ J/m^3. The anisotropic compression correction C_2 is usually much smaller in polymer networks, determined by secondary effects of non-Gaussian corrections and semi-softness. Since shear moduli C_i are much smaller than the bulk modulus C_3, polymer materials deform at essentially constant volume. A molecular theory of nematic elastomers [1] gives particular values to the shear moduli:

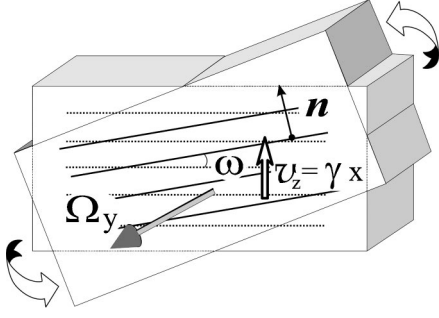$$C_1 = c_x k_B T, \quad C_2 = 0, \quad (3)$$

FIG. 2. The relative rotation coupling between the elastic matrix and the uniaxial layer system: the magnitude of local matrix rotation $\boldsymbol{\Omega} = \frac{1}{2} \text{curl } \boldsymbol{v}$ (or rather its component perpendicular to $\boldsymbol{n}$) has to be the same as the director rotation angle $\boldsymbol{\omega}$.

$$C_4 = \frac{1}{2} c_x k_B T, \quad C_5 = \frac{1}{2} c_x k_B T \frac{(r+1)^2}{r},$$

where $\mu = c_x k_B T$ is the rubber modulus in the isotropic phase (c_x proportional to the crosslinking density) and $r = l_\parallel / l_\perp$ is the anisotropy of polymer backbones forming the network, spontaneously liquid crystalline or with anisotropy induced by the mesophase.

When the variation of the principal anisotropy axis $\boldsymbol{n}$ is allowed, the coupling of the director fluctuations or induced rotations to the underlying rubbery network is described by two linear relative-rotation terms in the energy density:

$$F_{\text{rot}} = \frac{1}{2} D_1 [\boldsymbol{n} \times (\boldsymbol{\Omega} - \boldsymbol{\omega})]^2 + D_2 \, \boldsymbol{n} \cdot \underline{\underline{\tilde{\boldsymbol{\varepsilon}}}} \cdot [\boldsymbol{n} \times (\boldsymbol{\Omega} - \boldsymbol{\omega})], \quad (4)$$

where the small rotation vector $\boldsymbol{\omega}$ is a convenient measure of variation of the unit vector $\boldsymbol{n}$, $\boldsymbol{\omega} = [\boldsymbol{n} \times \delta \boldsymbol{n}]$. The elastic energy (4) arises when the director rotates differently from the underlying elastic matrix: at small deformations the latter rotation is often represented by a vector $\Omega_\alpha = \frac{1}{2} \epsilon_{\alpha\beta\gamma} \mathsf{v}_{\beta\gamma}$, or $\boldsymbol{\Omega} = \frac{1}{2} \text{curl } \boldsymbol{v}$, proportional to the antisymmetric part of strain $\mathsf{v}_{\beta\gamma}^A$. The orientations of $\boldsymbol{\omega}$ and $\boldsymbol{\Omega}$ are the axes of respective rotation in the two fields, $\mathbf{n}$ and $\boldsymbol{v}$, their magnitudes are the angles of these local rotations, see Fig. 2. First written by de Gennes on symmetry grounds [11], the relative-rotation coupling terms have been later obtained in the small-strain limit of the full microscopic theory, giving the particular values of the constants

$$D_1 = c_x k_B T \frac{(r-1)^2}{r}, \quad D_2 = c_x k_B T \frac{1-r^2}{r}. \quad (5)$$

As expected, in the isotropic limit $r \to 1$, both sets of constants, Eqs. (3) and (5), reduce to their values in classical Lamé elasticity, $D_1 = D_2 = 0$ and $C_1 = 2C_4 = 2C_5 = \mu$.

The relative-rotation coupling (4) penalizes local uniform director rotations with respect to the elastic matrix. For instance, if no elastic strain is allowed in the sample, this expression reduces to $F_{\text{rot}} = \frac{1}{2} D_1 (\delta \boldsymbol{n})^2$. Such a breaking of rotational invariance is not found in ordinary liquid crystals. There, like in standard linear elasticity, only the gradients of the deformation field contribute to the physical effects through the celebrated Frank curvature elastic energy density

$$F_{\text{Frank}} = \frac{1}{2} K_1 (\text{div } \delta \boldsymbol{n})^2 + \frac{1}{2} K_2 (\boldsymbol{n} \text{ curl } \delta \boldsymbol{n})^2$$
$$+ \frac{1}{2} K_3 [\boldsymbol{n} \times \text{curl} \delta \boldsymbol{n}]^2. \quad (6)$$

In most systems one finds the Frank constants $K_{1,2,3}$ of the same order of magnitude, crudely estimated as $\sim k_B T / a$ with a being a molecular length, giving $K \sim 10^{-11}$N [13]. The only real exception is main-chain liquid-crystalline polymers where, in the hairpin regime, the splay constant K_1 is much larger. We shall not consider such special cases here and will, therefore, assume that a physically important length scale, the elastic penetration depth $\xi = \sqrt{K/\mu}$, is a small quantity of order $\xi \sim 10^{-8}$ m.

B. Smectic energy density

Smectic or lamellar order is characterized by a 1D wave of density or composition, $\rho(z) \approx \rho_0 + |\psi| \cos(q_0 z + \Phi)$. Here z is measured along the layer normal, the amplitude of modulation $|\psi|$ is a critical function of temperature, $q_0 = 2\pi/d_0$ is the periodicity wave number, and $\Phi(\boldsymbol{r})$ an arbitrary phase [14]. Far below the smectic phase transition this modulation may be coarsened from the simple cosine form to a more steplike profile. Generally, from the symmetry point of view, the phase transition directly from the isotropic phase to smectic-A (a change between full rotational symmetry and the point-group $D_{\infty h}$ representing a simple cylinder) is exactly the same as that between the isotropic and nematic phases and it has to be first order. This is the case in many systems that are candidates for smectic elastomers, in particular—all lyotropic or block-copolymer lamellar phases. (A comprehensive description of symmetry changes during phase transformations in liquid crystals is given in Ref. [15].) The transition between an established nematic phase and smectic-A can, by symmetry, be second order. However, in practice, in the majority of ordinary liquid crystals with the I-N-A phase sequence, the N-A transition appears to be first order, cf. [13]. In contrast, in elastomers, due to the random-field effect of quenched crosslinks [8], one expects to find a continuous transition with $|\psi| \to 0$ much more frequently.

When the smectic order is well established, the phase of layer modulation can be written as $\Phi = -q_0 U(\boldsymbol{r})$ with $U(\boldsymbol{r})$ describing the layer displacement. Note the upper-case notation which, as in the case of network displacement $\boldsymbol{V}(\boldsymbol{r})$ in the previous section, includes both the *constant* displacement and the spatially varying part $u(\boldsymbol{r})$. The layer displacement is not a vector but only a component along the layer normal (z or $\boldsymbol{n}$ for the smectic A): displacements in the layer plane have no physical meaning for smectic liquid crystals. The continuum description of smectic and lamellar phases uses the gradients of nonuniform layer displacement $u(\boldsymbol{r})$ as effective strain fields, in this way any possible constant contribution to the displacement field U disappears from the analysis. As described in the following section, in a smectic rubber one finds a coupling of relative translations U and V_z, which is sensitive to their uniform parts as well. The correct elastic free energy must be invariant under the symmetry transformations of the phase, given here by the point-group $D_{\infty h}$, the 1D translational periodicity along z, and the condition of layer continuity. At leading order, the free-energy density of a smectic-A takes the classical form [13]

$$F_{\text{smA}} = \tfrac{1}{2} B (\nabla_z u)^2 + \tfrac{1}{2} K (\nabla_\perp^2 u)^2, \qquad (7)$$

where $\nabla_\perp^2 = \nabla_x^2 + \nabla_y^2$ describes the mean curvature of the layers, with the constant K equivalent to the splay Frank constant K_1 of a nematic and the B term penalizes the layer compression. The arguments leading to this expression, are made under the assumption that the nematic director $\boldsymbol{n}$ is always perpendicular to the layers, coinciding with the local layer normal $\boldsymbol{k}$. Usually, this is a fairly good approximation. However, close to the N-A transition, the constraint on $\boldsymbol{n}$ being perpendicular to layers becomes weaker and the director may independently fluctuate with respect to the layer normal. Strictly, even deep in the smectic-A phase, one should not regard the director as rigidly locked—it is just that deviations of $\mathbf{n}$ from $\mathbf{k}$ are penalized by a large energy.

One needs to examine how this nematic-smectic coupling affects the physical properties in corresponding elastomers. In particular, this is important because one expects the director fluctuations to be affected by the nematic relative rotation coupling to the rubbery network (4). The mean-field Landau free-energy density describing the N-A phase transition and the coupling to nematic director fluctuations is thoroughly discussed in the literature and summarized in monographs, e.g., [13]. The corresponding gradient terms describing the layer distortions are written as [14]

$$\widetilde{F}_{\text{smA}} = \tfrac{1}{2} g_\parallel q_0^2 |\psi|^2 (\nabla_z u)^2 + \tfrac{1}{2} g_\perp q_0^2 |\psi|^2 (\nabla_\perp u + \delta \boldsymbol{n})^2, \quad (8)$$

where the first term is the layer compression, leading directly to the B term in Eq. (7) with $B = g_\parallel q_0^2 |\psi|^2$. The second term, with $b_\perp = g_\perp q_0^2 |\psi|^2$, is the penalty for the deviation of local director $\delta \boldsymbol{n}$ from the locally rotated layer normal. The values $g_\parallel \neq g_\perp$ because of the uniaxial nematic anisotropy, but should be of the same order of magnitude. In a thermotropic smectic-A liquid crystal, the value for the layer compression constant is $B \geq 10^6$ J/m^3. One finds a similar value in lamellar block copolymers, while in diluted lyotropic lamellar systems, B can be much lower [16]. Another relevant length scale emerges from the smectic elastic energy density (7), the ratio $\sqrt{K/B} \simeq d_0$, giving the smectic layer spacing.

C. Relative translation coupling

The formation of a rubbery network in a smectic or lamellar phase results in preferential placement of crosslinks with respect to the layers. In the geometry of Fig. 1(c), the crosslinks are locked within the layer, as the real mesogenic side-chain polymers would indeed do. The sketch in Fig. 3 shows the crosslinks within the backbone in the interlayer spacing; in the synthetic work of Gebhard and Zentel [17] the crosslinking has been of this type. In any case there clearly is a barrier for a crosslinking ''point'' to instantly cross into the neighboring layer. Of course, crosslinks can freely migrate within their chosen layer plane. Accordingly, only the z component of the full crosslink displacement vector $\boldsymbol{V}$ participates in the relative translation coupling, shown in Fig. 3 and Eq. (9). Therefore, any attempt to deform the rubbery network (which amounts to the relative movement of crosslinks, described by the displacement vector $\boldsymbol{V}$, in-
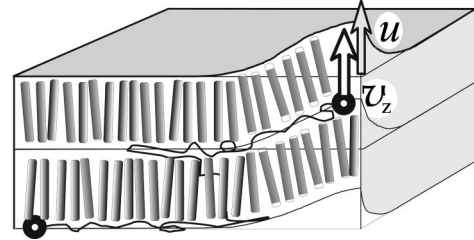

FIG. 3. The relative translation coupling: the movement of network crosslinks, locked with respect to the local smectic layer position, causes the layer distortion. The matrix displacement component along the layer normal V_z has to be the same as the local layer displacement U.

cluding the possible constant part) should produce an energy penalty, if the neighboring layers do not move in phase, see Fig. 3.

Unusually, such a coupling does not have to involve spatial gradients of the displacement fields $\boldsymbol{V}$ and U. In a traditional elastic continuum with only one relevant deformation field, $\boldsymbol{V}(\boldsymbol{r})$ or $U(\boldsymbol{r})$, the free energy cannot depend on such a field but only on its gradients, otherwise a constant displacement of the whole sample would cost energy. In nematic elastomers, because the second deformation field was orientational, we found a relative-rotation coupling of uniform fields of orientation. In a smectic system, with both deformation fields $\boldsymbol{V}$ and U corresponding to translations, we have an energy penalty on their local *relative* magnitude along the layer normal.

For small relative displacements between the layers and the elastic medium the penalty must be harmonic with a free-energy density of

$$F_{\text{trans}} = \Lambda \left[U(\boldsymbol{r}) - V_z(\boldsymbol{r}) \right]^2. \qquad (9)$$

Since no spatial derivatives are involved in Eq. (9) it is essential to separate the deformation fields U and V_z into their constant components, uniform (average) strains and fluctuations with respect to these average values, in both layer and elastomer subsystems. The analysis in Ref. [18] shows that there is a rigid constraint on the constant strains involving the displacement along the z axis, the layer normal. Essentially, an imposed uniform elastic shear v_{zx} or extension v_{zz} would result in a corresponding equal uniform layer rotation $\nabla_x u$ or extension $\nabla_z u$. In contrast, a shear or an extension in the layer plane, v_{xz} or v_{xx}, do not have such a direct effect on the layers. In this paper we do not consider such imposed shears and mostly concentrate on the fluctuations and effective elastic constants. Therefore, the harmonic coupling of local fluctuations $\Lambda [u - v_z]^2$ will be sufficient in most cases.

In a continuum theory one requires an estimate for the new coupling constant Λ. Equation (9) describes an effect combining the entropic rubber elasticity and the smectic layer potential barrier, hence the characteristic energy scale is $\alpha(\psi) k_B T$. Here α is an unknown coefficient of order unity, which however must depend on the smectic order parameter $|\psi|$, tending to zero near a transition. The continuum model of a rubbery network has a short distance cutoff at R_0, the characteristic distance between connected crosslinking points (the spatial extent of elastically active network strands). Taking into account the number of network strands

per unit volume c_x, we can write on the grounds of dimensional analysis $\Lambda \approx \alpha c_x k_B T / R_0^2$ (compare with the rubber modulus $\mu = c_x k_B T$). Since chain configurations in the rubbery state are random walks, we have roughly $c_x \sim (l R_0^2)^{-1}$, with l being the characteristic step length of such a walk. Thus Λ may be further written as $\sim k_B T / (l R_0^4)$. In a typical polymer the step length $l \sim 1$ nm. Therefore, in a rubber material with modulus $\mu \sim 10^5$ J/m^3 at room temperature ($k_B T \sim 4 \times 10^{-21}$ J) the characteristic network span should be $R_0 \sim 6-10$ nm and the constant $\Lambda \sim 2.5 \times 10^{21}$ J/m^5.

On the grounds of symmetry we might wish to write another coupling term. It is also due to the translational symmetry breaking of layers and should take the form $\Delta_0 (\tilde{\varepsilon}_{zz} - \nabla_z u)^2$. Such contribution to the energy density describes the evident fact that, when the material is stretched along the layer normal z, the layer spacing has to stretch too, deviations being penalized by an energy of order Δ_0. However, such coupling serves a minor role, being a small addition to a far more important effect—the relative translation coupling (9) leading to a rigid locking of uniform z strains.

III. THE CALCULATION

The full free-energy density, expressed as a sum of all the contributions discussed above, Eqs. (1), (4), (6), (8), and (9), contains several independent degrees of freedom: the local displacement of elastic network $v(r)$, the layer displacement $u(r)$, and the nematic director $n(r)$. These fields fluctuate independently and couple to each other in the free energy, thus affecting the macroscopic response of the system. In order to calculate such responses, e.g., an effective elastic modulus, one needs to minimize the total free energy with respect to all other degrees of freedom, in this case—the director and the layer fields. In other words, in order to compute a given macroscopic property of a system with microstructure, one has to integrate out the fluctuations of this microstructure.

In the first instance, we would like to perform the integration over nematic director modes and find the effective free-energy density of smectic and elastic fields $v(r)$ and $u(r)$, for which the director has found a corresponding lowest-energy strain configuration. The equilibrium properties of a system are determined by the full partition function $\mathcal{Z} = \int \mathcal{D}n\, \mathcal{D}u\, \mathcal{D}v \exp[-(1/k_B T)\mathcal{H}(n,u,v)]$ with the director-dependent part of $\mathcal{H}$ given by all contributions discussed in the last section. Carrying out the first step, the integration over director fluctuation modes δn, one may use the method of steepest descent, which is equivalent to minimization $\delta \mathcal{H}/\delta n = 0$ at fixed $u(r)$ and $v(r)$, and leads to the "effective Hamiltonian" depending only on these remaining fields. This section outlines several examples of such computation.

In linear continuum theory, where the free energy is typically a quadratic form in the fluctuating fields, the steepest-descent method is giving an exact result and, therefore, the "integrating out of the fluctuating degrees of freedom" is mathematically equivalent to the minimization of $\mathcal{H}(n,u,v)$. This is most easily done in reciprocal space, enabling one to perform the minimization by algebraic manipulations rather than by solving differential Euler-Lagrange equations. Following the review article [14], it is convenient to switch into
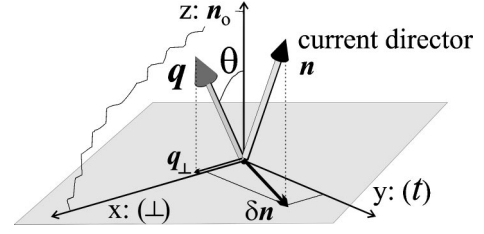

FIG. 4. Geometry of relevant vectors in the problem. The principal axis z is chosen along the initial n_0, with the director deviation δn perpendicular to it. Two arbitrary axes in the x-y plane are chosen along the projection of the wave vector $q_\perp$ (axis $\perp$) and perpendicular to it (the transverse axis t).

a cylindrical polar notation with the principal axis along the initial nematic director, see Fig. 4.

We denote the direction parallel to the initial director n_0 (and the smectic layer normal) as $\parallel$ or z. At a point in reciprocal space q we denote the direction parallel to $[n_0 \times [q \times n_0]]$ by $\perp$. The orthogonal direction in the x-y plane, parallel to $[n_0 \times q]$ is denoted by t (for transverse), see Fig. 4. All vectors in our new reciprocal space coordinate system can now be expressed in terms of the unit vectors $e_z(q)$, $e_\perp(q)$, and $e_t(q)$.

A. Integrating out the nematic director δn

At the first instance, we are interested only in the role of director fluctuations $\delta n(r)$, as the field that does not have a relevance for macroscopic observable properties of smectic rubber. Performing the Fourier transformation of those parts of free-energy density that involve δn, one obtains a free-energy density in q space

$$F_q = \tfrac{1}{2}(D_1 + b_\perp + K_1 q_\perp^2 + K_3 q_z^2)|\delta n_{q\perp}|^2$$
$$+ \tfrac{1}{2}(D_1 + b_\perp + K_2 q_\perp^2 + K_3 q_z^2)|\delta n_{qt}|^2$$
$$+ \tfrac{1}{2}(Bq_z^2 + b_\perp q_\perp^2)|u_q|^2 + \tfrac{1}{4}(iq_\perp[D_1 + D_2]\,\delta n_{q\perp} v_{qz}^*$$
$$+ 2iq_\perp b_\perp \delta n_{q\perp} u_q^* + \text{c.c.})$$
$$- \tfrac{1}{4}(D_1 - D_2)[iq_z(\delta n_{q\perp} v_{q\perp}^* + \delta n_{qt} v_{qt}^*) + \text{c.c.}], \quad (10)$$

where all three fields are complex functions of the wave vector q; c.c. stands for complex conjugate combinations explicitly arising in the coupling terms. Note that in an ordinary smectic liquid (with no background rubbery network) the relative-rotation constants D_1 and D_2 are zero and the only addition to the Frank elasticity is the term proportional to $b_\perp = g_\perp q_0^2 |\psi|^2$.

The optimal values for two components $\delta n_{q\perp}$ and δn_{qt} are obtained from the quadratic forms in Eq. (10):

$$\delta n_{qt} = \frac{i}{2}\frac{(D_2 - D_1)q_z v_{qt}}{D_1 + b_\perp + K_2 q_\perp^2 + K_3 q_z^2}, \quad (11)$$

$$\delta n_{q\perp} = \frac{i}{2}\frac{(D_2 - D_1)q_z v_{q\perp} + (D_2 + D_1)q_\perp v_{qz} + 2b_\perp q_\perp u_q}{D_1 + b_\perp + K_1 q_\perp^2 + K_3 q_z^2}.$$

In the limiting case when the crosslinking density of the network is zero, i.e., there is no underlying rubber-elastic matrix, Eqs. (11) reduce to

$$\delta \boldsymbol{n}_{\boldsymbol{q}\, t} = 0; \quad \delta \boldsymbol{n}_{\boldsymbol{q}\perp} \approx i\, q_{\perp} u_{\boldsymbol{q}}$$

after expansion at small wave vector $\boldsymbol{q}$ (continuum deformations are at $|\boldsymbol{q}| \ll \sqrt{b_{\perp}/K_{1,3}}$ below the N-A transition where $b_{\perp} \neq 0$). In real space this gives, explicitly, $\delta \boldsymbol{n} \approx -\boldsymbol{\nabla}_{\perp} u$, that is the average director is tied to the layer normal and rotates with it on deformations. In this case the effective smectic elastic free-energy density takes the form

$$F_{\text{smA}} = \tfrac{1}{2}(B q_z^2 + K_1 q_{\perp}^4)|u_{\boldsymbol{q}}|^2, \tag{12}$$

which is the Fourier transform of Eq. (7), the elastic energy of a lamellar phase. We see that it is indeed the splay Frank constant K_1 of an underlying nematic that controls the layer curvature term, proportional to the fourth-order gradient $q_{\perp}^4$. We shall see below that the coupling to a rubbery network removes this degeneracy.

Substituting the optimal director modes (11) into Eq. (10) and only retaining the leading terms in powers of the small wave vector $\boldsymbol{q}$, we have

$$
\begin{aligned}
F_q = {} & \frac{1}{2} B q_z^2 |u_{\boldsymbol{q}}|^2 + \frac{b_{\perp} D_1}{2(b_{\perp}+D_1)} q_{\perp}^2 |u_{\boldsymbol{q}}|^2 \\
& + \left(\frac{b_{\perp}^2}{2(b_{\perp}+D_1)^2} K_1\, q_{\perp}^4 |u_{\boldsymbol{q}}|^2 \right) \\
& + \frac{[b_{\perp}(D_1-2D_2)-D_2^2]}{8(b_{\perp}+D_1)} q_z^2 (|v_{\boldsymbol{q}\perp}|^2+|v_{\boldsymbol{q}\, t}|^2) \\
& + \frac{[b_{\perp}(D_1+2D_2)-D_2^2]}{8(b_{\perp}+D_1)} q_{\perp}^2 |v_{\boldsymbol{q}\, z}|^2 \\
& - \frac{(b_{\perp} D_1 + D_2^2)}{4(b_{\perp}+D_1)} q_{\perp} q_z \tfrac{1}{2}[v_{\boldsymbol{q}\perp}^* v_{\boldsymbol{q}\, z} + v_{\boldsymbol{q}\, z}^* v_{\boldsymbol{q}\perp}] \\
& - \frac{b_{\perp}(D_1+D_2)}{2(b_{\perp}+D_1)} q_{\perp}^2 \tfrac{1}{2}[u_{\boldsymbol{q}}^* v_{\boldsymbol{q}\, z} + v_{\boldsymbol{q}\, z}^* u_{\boldsymbol{q}}] \\
& + \frac{b_{\perp}(D_1-D_2)}{2(b_{\perp}+D_1)} q_{\perp} q_z \tfrac{1}{2}[u_{\boldsymbol{q}}^* v_{\boldsymbol{q}\perp} + v_{\boldsymbol{q}\perp}^* u_{\boldsymbol{q}}]. \tag{13}
\end{aligned}
$$

The K_1 term is placed in parentheses as it is fourth order in $\boldsymbol{q}$. We retain it to illustrate how it would give the $K q_{\perp}^4$ in a normal smectic phase where this represents the leading effect in the layer plane.

Bringing this result together with other contributions to full free energy, which did not contain the fluctuating $\delta \boldsymbol{n}$, one obtains the effective energy density of a smectic elastomer depending only on the elastic and layer displacements. The expression is then converted into real space by matching the coefficients of the various combinations allowed by symmetry:

$$F = F_{\text{el}} + F_{\text{smA}} + F_{\text{coupling}}. \tag{14}$$

The rubber-elastic part F_{el} is determined by the same five-constant expression, Eqs. (1) and (2), which is dictated by the uniaxial symmetry. The only modification is the renormalized value of the shear modulus
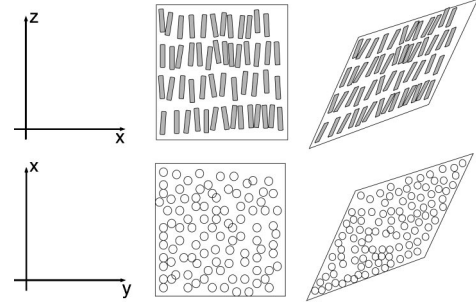

FIG. 5. Shearing in x-z plane governed by the modulus C_5 and shearing in x-y plane governed by C_4 clearly show how the layer structure affects the elastic response in the first case but does not in the second.

$$C_5^{\text{smA}} = C_5 - \frac{D_2^2}{8(b_{\perp}+D_1)}. \tag{15}$$

This is exactly what one would expect physically, see Fig. 5, as shear in the z-x plane implies a rotation of the director with respect to the layers and the elastic matrix. In contrast, for the x-y shear corresponding to the coupling constant C_4 also pictured in Fig. 5, the director takes a purely passive role and thus this constant is not renormalized. Note that in the pure nematic case the analogous renormalization by director fluctuations is the combination $C_5 - \frac{1}{8} D_2^2/D_1 \to 0$, first obtained by Olmsted in a study of soft elasticity in nematic rubbers [2]. Clearly, the coupling to smectic layers imposes sufficient constraints on director fluctuations to prevent the complete softness. As expected, the resulting correction away from softness is then proportional to the degree of smectic order, via the order parameter dependence $b_{\perp} \sim |\psi|^2$.

The smectic energy density F_{smA} can be brought to the standard form, Eq. (7), with a renormalized layer-curvature constant:

$$K = \frac{b_{\perp}^2}{2(b_{\perp}+D_1)^2} K_1. \tag{16}$$

Finally, the coupling between the rubber-elastic and smectic layer deformations in Eq. (14) takes the explicit form, combining the terms of corresponding symmetry with $u(\boldsymbol{r})$ and $\boldsymbol{v}(\boldsymbol{r})$,

$$
\begin{aligned}
F_{\text{coupling}} = {} & \Lambda[V_z(\boldsymbol{r}) - U(\boldsymbol{r})]^2 + \tfrac{1}{2}\Delta_1[(\boldsymbol{\Omega}-\boldsymbol{\omega}_{\text{A}})\times \boldsymbol{n}_0]^2 \\
& + \Delta_2\, \boldsymbol{n}_0 \cdot \widetilde{\boldsymbol{\varepsilon}} \cdot [(\boldsymbol{\Omega}-\boldsymbol{\omega}_{\text{A}})\times \boldsymbol{n}_0] \\
= {} & \Lambda[V_z(\boldsymbol{r}) - U(\boldsymbol{r})]^2 + \tfrac{1}{2}\Delta_1(\mathsf{v}_{iz}^A + \nabla_i u)^2 \\
& + \Delta_2\, \varepsilon_{zi}(\mathsf{v}_{iz}^A + \nabla_i u), \tag{17}
\end{aligned}
$$

with the summation over $i = x, y$, where $\boldsymbol{\omega}_{\text{A}}$ is the vector describing the local layer rotation, with components to first order $\boldsymbol{\omega}_{\text{A}} = (\boldsymbol{\nabla}_y u, -\boldsymbol{\nabla}_x u, 0)$. Here one finds an important contrast with the ordinary smectic expression (7). To illustrate the point, consider the case when no elastic strains are permitted in the rubbery network. At $\boldsymbol{v} = 0$, Eq. (17) reduces to

$$F_{\text{coupling}} \rightarrow \Lambda\, (u)^2 + \tfrac{1}{2}\Delta_1(\boldsymbol{\nabla}_\perp u)^2.$$

Both terms significantly impede fluctuations of smectic layers. For instance, the familiar degeneracy (the leading $q_\perp^4$ dependence) is not obtained in the corresponding lamellar rubbery network. In Sec. IV we shall examine this effect in greater detail, taking into account the effect of a fluctuating, rather then zero, elastic field $\boldsymbol{v}(\boldsymbol{r})$.

The coupling constants are now given by the combination of underlying nematic relative rotations and the smectic parameter $b_\perp \sim |\psi|^2$:

$$\Delta_1 = \frac{b_\perp D_1}{b_\perp + D_1} \quad \text{and} \quad \Delta_2 = \frac{b_\perp D_2}{b_\perp + D_1}. \qquad (18)$$

In addition to the relative translation term, unique to smectic phases, the Δ_1 coupling penalizes relative rotation of the layers and the elastic matrix, and the Δ_2 term couples relative rotations to symmetric strains of the matrix. When the nematic director is very strongly anchored along the layer normal, the nematic relative rotation ($D_{1,2}$) is really equivalent to that of a smectic. Accordingly, we may notice that if $b_\perp \gg D_1$, there is such an equivalence emerging from expressions (18). In the opposite limiting case, when the network is rather rigid and smectic layers present a weaker influence, $D_1 \gg b_\perp$ (which should also be the case near the N-A phase transition when $|\psi| \rightarrow 0$), one obtains a correspondingly weaker coupling, $\Delta_1 = b_\perp$; $\Delta_2 = b_\perp (D_2/D_1)$.

This section presents a consistent continuum elastic theory of linear elasticity in rubber networks with smectic or lamellar order. All expressions are derived phenomenologically. To complete this description, it is useful to present the effective elastic and coupling constants that derive from the underlying nematic elastomer—for which there exists a molecular-level description, e.g., see the review [1]. This would also allow some predictive power in estimates of magnitude of these constants. The constants follow from Eqs. (3)–(5). For a uniaxial smectic-A rubber one obtains

$$C_1 = 2C_4 = c_x k_B T, \quad C_2 = 0,$$

$$C_5^{\text{smA}} = \frac{1}{8}\frac{b_\perp c_x k_B T\,(r+1)^2}{c_x k_B T\,(r-1)^2 + b_\perp r},$$

$$\Delta_1 = \frac{b_\perp c_x k_B T\,(r-1)^2}{c_x k_B T\,(r-1)^2 + b_\perp r},$$

$$\Delta_2 = \frac{b_\perp c_x k_B T\,(1-r^2)}{c_x k_B T\,(r-1)^2 + b_\perp r}. \qquad (19)$$

Near the nematic-smectic phase transition, when $b_\perp = g_\perp q_0 |\psi|^2$ decreases as $|\psi| \rightarrow 0$, the renormalized shear modulus $C_5^{\text{smA}} \approx \frac{1}{8}b_\perp(r+1)^2/(r-1)^2$. Deep in the smectic phase, at $|\psi| \rightarrow 1$, we can assume that the magnitude of $b_\perp$ is not very different from the layer compression constant $B = g_\parallel q_0 |\psi|^2 \sim 10^6$ J/m^3 in a typical smectic system, which is usually much greater than $\mu = c_x k_B T$. In this case the shear modulus recovers its ''bare'' value, as given by the original expression for a nematic rubber: $C_5^{\text{smA}} \approx \frac{1}{8}c_x k_B T\,(r+1)^2/r$.

Similarly, at $|\psi| \rightarrow 1$, the model expressions for the smectic-rubber coupling constants approach the (large) values characteristic of a nematic elastomer $|\Delta_{1,2}| \rightarrow |D_{1,2}|$. When the smectic or lamellar order is weak, $b_\perp, |\psi| \rightarrow 0$, these coupling constants are proportional to $b_\perp$.

It is also interesting to discuss the case of an elastomer with lamellar microstructure, which does not have an underlying nematic order: a lyotropic lamellar phase, or a microphase separated block-copolymer crosslinked into a rubbery network. The analysis of this section, including the free-energy density expressions (14) and the relations between the moduli, remain valid. However, the backbone chain anisotropy $(r-1) = (l_\parallel/l_\perp - 1)$, which is a measure of ''nematic order parameter'' Q, is now directly given by the emerging lamellar density modulation: $Q \sim |\psi|^2$. One then might expect unusual mechanical anomalies when the ratio $b_\perp/(r-1)^2 \sim 1/|\psi|^2$ may actually grow near the transition. There will be no physical divergence since the transition directly from isotropic into the smectic phase has to be first order, by symmetry. Nevertheless, a substantial hardening of certain mechanical modes may be registered as a lamellar rubber approaches its isotropic phase.

B. Integrating out the layer structure

We now proceed to integrate out the fluctuations of the layer structure, in a similar fashion to the previous section. We would thus like to determine the effective mechanical response of a smectic rubber when the layers are allowed to fluctuate freely and adopt the optimal conformation that lowers the total free energy (14). The effective equilibrium rubber-elastic energy is obtained by integrating out the layer fluctuation modes in reciprocal space, $u(\boldsymbol{q})$ with zero mean. Strictly, the result of such optimization depends on the magnitude and geometry of imposed strains $\tilde{\varepsilon}_{ij}$, externally applied to the sample. However, we are presently only interested in effective rubber-elastic moduli, which are determined by the effective *equilibrium* energy with no externally imposed deformations. The result of such calculation should be quite general and, again, equally applicable to thermotropic smectic-A elastomers, lyotropic lamellar gels of crosslinked polysurfactants, and lamellar phases of block copolymers.

We write the Fourier transform of the free-energy density and then minimize it with respect to the smectic layer fluctuation modes $u(\boldsymbol{q})$. In the leading approximations of expansion at small wave vectors, the resulting optimal layer modes are given by

$$u_{\boldsymbol{q}} = v_{\boldsymbol{q}z} - \frac{B}{2\Lambda}q_z^2 v_{\boldsymbol{q}z} - \frac{(\Delta_1 - \Delta_2)}{4\Lambda}q_\perp(q_\perp v_{\boldsymbol{q}z} + q_z v_{\boldsymbol{q}\perp}) + \cdots,$$

$$u(\boldsymbol{r}) \approx v_z + \frac{B}{2\Lambda}\left(\frac{\partial \varepsilon_{zz}}{\partial z}\right) + \frac{(\Delta_1 - \Delta_2)}{2\Lambda}\left(\frac{\partial \varepsilon_{xz}}{\partial x} + \frac{\partial \varepsilon_{yz}}{\partial y}\right). \qquad (20)$$

The parameter of such expansion is, as one can see from the ratio of terms in Eq. (20), $\sim (B/\Lambda)q_z^2$ or $(\mu/\Lambda)q_\perp^2$. For the second term it is straightforward to check that the series expansion is valid when $q_\perp \ll 1/R_0$, the inverse network span, which should be easily satisfied in any practical situation.

The relation is less obvious, and the condition on the long wavelength more demanding, for deformations along the layer normal because one often finds a large layer compression constant, $B \gg \mu$, especially in weakly crosslinked gels. The corrections to $u \approx v_z$ would become relevant for deformations along z with wavelength $\geqslant \sqrt{\Lambda/B}$.

Putting the optimal value for the layer fluctuation mode back to Eq. (14) and rearranging the terms, one obtains the effective elastic energy density of a smectic elastomer in the form of F_{el} of the Eqs. (1) and (2). Of course, nothing else but the same five elastic terms in the uniaxial medium could have been expected on the symmetry grounds. The rubber elastic constants are renormalized by smectic fluctuations and acquire the effective values:

$$\text{Bulk moduli} \quad C_3^{\mathrm{eff}} = C_3 + \tfrac{1}{18}B, \quad C_2^{\mathrm{eff}} = C_2 + \tfrac{1}{6}B,$$

$$\text{Shear moduli} \quad C_1^{\mathrm{eff}} = C_1 + \tfrac{1}{2}B, \quad C_4^{\mathrm{eff}} = C_4,$$

$$C_5^{\mathrm{eff}} = C_5^{\mathrm{smA}} + \tfrac{1}{8}(\Delta_1 - 2\Delta_2), \tag{21}$$

where C_5^{smA} is given by expression (15) and, of course, one can safely neglect the correction to the main bulk modulus C_3.

To complete, and again make a connection with the molecular theory of nematic elastomers, let us present the effective rubber moduli of a smectic elastomer through the model microscopic expressions (3)–(5). We thus obtain

$$C_1^{\mathrm{eff}} = \tfrac{1}{2}B + c_x k_B T, \quad C_2^{\mathrm{eff}} = \tfrac{1}{6}B,$$

$$C_4^{\mathrm{eff}} = \tfrac{1}{2}c_x k_B T, \quad C_5^{\mathrm{eff}} = \tfrac{1}{2}\frac{b_\perp r^2 c_x k_B T}{c_x k_B T (r-1)^2 + b_\perp r}. \tag{22}$$

As before, near the nematic-smectic phase transition the shear modulus $C_5^{\mathrm{eff}} \sim b_\perp \to 0$. Deep in the smectic phase $C_5^{\mathrm{eff}} \to c_x k_B T (r/2)$.

The most important effect is the asymmetric renormalization of the shear moduli C_1 and C_4. Taking a typical smectic value $B \sim 10^6$ J/m^3, much greater than a typical $c_x k_B T \sim 10^4 - 10^5$ J/m^3, one finds the effective modulus $C_1 \gg C_4$ in a thermotropic smectic elastomer.

Appendix A gives details of calculation of the two effective elastic response moduli, $\mu_\parallel$ and $\mu_\perp$, that determine the force on stretching the smectic elastomer along, and perpendicular to the layer normal z. These cases are shown in Figs. 6(a) and 6(b). An isotropic rubber stretched by an amount ε in one direction contracts symmetrically by $-\tfrac{1}{2}\varepsilon$ in the two perpendicular directions (or λ and $1/\sqrt{\lambda}$ in terms of Cauchy strains) and responds with a modulus $\mu_0 = 3 c_x k_B T$. On stretching the monodomain smectic in the layer plane (ε_{xx} imposed) the elastic response is given by the modulus

$$\mu_\perp = \frac{8 C_4 (C_1 + C_4)}{C_1 + 2 C_4} \to 8 C_4 \sim 4 c_x k_B T,$$

a usual rubber-elastic shear scale. The incompressibility-driven contraction along the layer normal z is resisted by the effective modulus $\sim C_5 \simeq B$, insisting that the layer spacing d_0 remains constant. Because the ratio of the effective moduli is large, no noticeable contraction along the layer
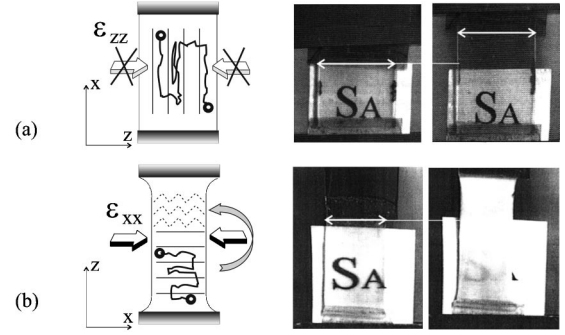

FIG. 6. Stretching the monodomain smectic elastomer (vertical in both sketches and images): imposed strain (a) ε_{xx}—in the layer plane, vertical in the picture and (b) ε_{zz}—along the layer normal. In the first case the high-modulus resistance to layer compression prevents the sample from changing its z dimension. In the second case the directions perpendicular to the imposed strain offer no such resistance and $\varepsilon_{xx} \approx -\tfrac{1}{2}\varepsilon_{zz}$. This holds for small strains. However, at a higher strain the smectic finds a lower-energy deformation path: layer buckling via the Helfrich-Hurault instability. The images are courtesy of Nishikawa and Finkelmann.

normal would take place: $\varepsilon_{zz} \to 0$, see Fig. 6(a). Therefore, the sample thickness (into the page in Fig. 6) must decrease more: $\varepsilon_{yy} \to -\varepsilon_{xx}$.

In the reverse situation, when the sample is stretched along the layer normal (ε_{zz} imposed) the measured effective modulus is

$$\mu_\parallel = 2(C_1 + C_4) \to 2 C_1 \sim B,$$

much higher than a normal rubber response. Both perpendicular directions in the layer plane are now equivalent and experience the usual volume conserving contraction $\varepsilon_{yy} = \varepsilon_{xx} = -\tfrac{1}{2}\varepsilon_{zz}$. In this geometry, however, the material will be able to find a lower-energy deformation mode: the Helfrich-Hurault type of layer buckling instability discussed in a number of papers [13,19,20] and resulting in an optically opaque scattering state in experiments [21,22], see Fig. 6(b).

IV. LAYER STRUCTURE IN SMECTIC ELASTOMERS

We now continue to study the properties of smectic elastomers in equilibrium, when no external deformation is applied and the sample preserves its overall shape. In the previous section we obtained effective rubber-elastic moduli, which were renormalized by the freely fluctuating smectic layers whose only constraint was the coupling to the polymer network.

Let us examine the opposite strategy. The smectic-layer degree of freedom $u(\mathbf{r})$ can be easily monitored and is often the subject of an experimental study by optical or x-ray methods. The reason for this interest, apart from the practical attraction in manipulating the optical birefringence, is the fundamental problem of the thermodynamics of a one-dimensional crystalline lattice. The problem can be summarized as follows. A translational symmetry breaking in one dimension only (i.e., a system of parallel equidistant layers with no interlayer structure: a smectic-A) has, by symmetry, the degenerate elastic energy density expressed by Eq. (7) or (12) in real and Fourier space, respectively. Assuming rea-

sonably long-wavelength deformations, the equipartition theorem of thermodynamics tells us that each mode of layer fluctuation $u(\boldsymbol{q})$ has a mean-square average

$$\langle |u_q|^2 \rangle = \frac{V k_B T}{B\, q_z^2 + K\, q_\perp^4}. \tag{23}$$

Since layer fluctuations in the plane are penalized by a higher power of displacement gradient, the fluctuation modes have a much higher amplitude at $q \to 0$ than in a usual three-dimensional solid (where the analogous mean-square average is proportional to $k_B T / C\, q^2$). The quality of order in a lattice is determined by the correlation of its fluctuations in real space. In a smectic one-dimensional lattice such fluctuations correlate over large distances: a direct integration gives, e.g., [24],

$$\langle u(0) u(\boldsymbol{r}) \rangle = \int \frac{k_B T}{B\, q_z^2 + K q_\perp^4}\, e^{-i(\boldsymbol{q}\cdot\boldsymbol{r})}\, \frac{d^3 q}{(2\pi)^3}$$

$$\sim \begin{cases} \dfrac{k_B T}{(B\, K)^{1/2}} \ln(r_z) & \text{if } r_\perp = 0 \\[2ex] \dfrac{k_B T}{(B\, K)^{1/2}} \ln(r_\perp) & \text{if } r_z = 0. \end{cases} \tag{24}$$

This weak logarithmic divergence is known as the Landau-Peierls effect. It corresponds to the slow, power-law decay of the structure factor $\mathcal{S}(r)$, defined here as the correlation of density fluctuations, $\langle \exp(i q_0 [u(r) - u(0)]) \rangle = \exp(-\frac{1}{2} q_0^2 \langle [u(r) - u(0)]^2 \rangle)$, with the wave vector $q_0 = 2\pi/d_0$, and signifies the marginal case between the true crystalline or bond orientational order, with the structure factor constant as $r \to \infty$, and a short-range order of liquids with rapidly decaying $\mathcal{S}(r) \sim e^{-r/\xi}$.

Such an effect is directly seen on x-ray scattering experiments, where the diffraction from smectic layer density modulation generates a peak in reciprocal space at $q_\circ = 2\pi/d_0$. The scattering intensity $I(q)$ is proportional to the Fourier transform of $\mathcal{S}(r)$ and thus reflects the nature of correlations in the system. In a crystalline lattice with long-range order, the Bragg reflections are nominally delta functions, $I(q) \sim \delta(q - q_0)$ at each reciprocal lattice vector [23], which are broadened by the diffusive scattering and modulated by the Debye-Waller factor $\sim \exp[-\pi^2 k_B T / d_0^3 C]$, a measure of thermal fluctuations. Quasi-long-range order in a one-dimensional smectic lattice results in the famous expression for the scattering intensity [24]

$$I_n(q_z, q_\perp = 0) \sim \frac{1}{(q_z - n q_0)^{2 - \eta n^2}}$$

and

$$I(q_z = 0, q_\perp) \sim \frac{1}{q_\perp^{4 - 2\eta n^2}}. \tag{25}$$

The anisotropic power-law decay describes the intensity around the peak position, near the nematic-smectic transition

with the exponent $\eta(T) = (1/8\pi) q_0^2 (k_B T / \sqrt{B\, K})$. When $\eta n^2 > 2$ there is no singularity in the scattering intensity at all. Thus high-order peaks are suppressed and in fact usually only the first-order peak is observed experimentally. Precision x-ray scattering experiments, beginning from the work of Als-Nielsen et al. [25–27], have confirmed this prediction and the following critical behavior of smectic liquid crystals, dominated by thermal fluctuations. We expect that in smectic elastomers and gels, due to the coupling to the rubbery network, these fluctuations will be reduced. We shall see that the elastic matrix of the smectic elastomers reestablishes long-range order so fluctuations merely attenuate the full range of Bragg scattering peaks.

Similar to the treatment in the previous section, we need to find an effective Hamiltonian of the smectic elastomer system, described by the layer phase variable $u(\boldsymbol{r})$ or its Fourier modes $u(\boldsymbol{q})$. To do this, we need to integrate out the unconstrained fluctuations of the elastic deformation field $\boldsymbol{v}(\boldsymbol{q})$—the phonon modes in the equilibrium rubbery network. We consider mechanically undistorted elastomers: the results are different when an elastic strain is imposed in the system and will be reported in a different publication.

The details of the calculation are given in Appendix B. The Fourier transform of the free-energy density (14), which depends on both $\boldsymbol{v}(\boldsymbol{q})$ and $u(\boldsymbol{q})$, can be arranged as a quadratic form:

$$F = \tfrac{1}{2} \boldsymbol{v}_q \cdot \underline{\boldsymbol{G}}(\boldsymbol{q}) \cdot \boldsymbol{v}_q^* - \boldsymbol{\Gamma}(\boldsymbol{q}) \cdot [\boldsymbol{v}_q u_q^* + \boldsymbol{v}_q^* u_q] + \tfrac{1}{2} \mathcal{M}(\boldsymbol{q}) |u_q|^2. \tag{26}$$

The optimal modes of network deformations $\boldsymbol{v}_q$ are obtained by minimization of this quadratic form producing a vector displacement of $\boldsymbol{v}_q = 2(\underline{\boldsymbol{G}}^{-1} \cdot \boldsymbol{\Gamma}) u_q$, which is rather cumbersome. We examine the expression as an illustration in the limit $q_z / q_\perp \ll 1$, that is for modes that lay almost along the plane of the layers:

$$v_{q z} \approx \left[1 + \frac{1}{8\Lambda}(\Delta_1 - 8 C_5) q_\perp^2 + \frac{1}{4\Lambda}(\Delta_1 - \Delta_2) q_z^2 + \cdots \right] u_q,$$

$$v_{q \perp} \approx \left\{ \left[1 - \frac{1}{8\Lambda}(\Delta_1 + \Delta_2) q_\perp^2 \right] (q_z / q_\perp) + \cdots \right\} u_q,$$

$$v_{q t} = 0. \tag{27}$$

This shows the expected behavior, that for small $\boldsymbol{q}$, one obtains $v_z = u$, that is the normal displacement of the elastic matrix becomes rigidly fixed to layers. Also in the same limit $v_{q \perp} = (q_z / q_\perp) u_q$, $v_{q t} = 0$ or in real space $\partial v_x / \partial x = \partial u / \partial z$, $v_t = 0$ showing that the material appears incompressible to these modes.

The effective free-energy density, evaluated at the optimal configuration of network phonons, and simplified as described in Appendix B, becomes

$$F^{\text{eff}} \approx \frac{1}{2} \left[\frac{8C_5^{\text{eff}} q_z^4 + (8C_5^{\text{smA}} - 3\Delta_1 - 2\Delta_2) q_\perp^4 - 2(2\Delta_1 - 2\Delta_2) q_z^2 q_\perp^2}{4q_\perp^2 + (4C_5^{\text{eff}}/C_3) q_z^2 + (4C_5^{\text{eff}}/\Lambda) q_z^4} + Bq_z^2 \right] |u_q|^2,$$

where

$$C_5^{\text{eff}} = C_5^{\text{smA}} + \tfrac{1}{8}(\Delta_1 - 2\Delta_2), \tag{28}$$

cf. Eq. (21). Note that the term $\sim (C_5/C_3) q_z^2$ in the denominator cannot be neglected in spite of the nominal incompressibility. One may encounter a situation when $q_\perp = 0$, when this term will become the leading effect. Expression (28) may still appear cumbersome, but it is easy to study its implications in the two limiting cases, $q_z \to 0$ and $q_\perp \to 0$ separately. These two limits, in which the results can be presented in a simple intuitive way, are also the focus of the classical theories and experiments on smectic-A liquid crystals. The mean-square layer fluctuation, remaining after the elastomer penalty has been implemented, follows directly from Eq. (28). The result depends on the orientation of the fluctuation mode.

In the most common case $q_\perp/q_z \gg \sqrt{C_5/C_3}$ the bulk modulus C_3 cancels from the numerator and denominator in Eq. (28), giving:

$$\langle |u(\boldsymbol{q})|^2 \rangle_\perp \approx \frac{V k_B T}{B^* q_z^2 + 2C_5^* q_\perp^2 + 2C_5^{\text{eff}}[q_z^4/q_\perp^2]} = \frac{V k_B T}{q^2} \frac{\sin^2 \theta}{2C_5^{\text{eff}} + (B^* - 4C_5^{\text{eff}})\sin^2 \theta - (B^* - 2C_5^{\text{eff}} - 2C_5^*)\sin^4 \theta},$$

where

$$B^* = B - \Delta_1 + \Delta_2, \quad C_5^* = C_2^{\text{smA}} - \tfrac{1}{8}(3\Delta_1 + 2\Delta_2) \tag{29}$$

and $\theta \gg \sqrt{C_5/C_3}$ is the angle between the wave vector of deformation $\boldsymbol{q}$ and the layer normal z, see Fig. 4. One can verify that the kernel of Eq. (28) and the denominator of Eq. (29) are positive for all directions of $\boldsymbol{q}$, even though some combinations of B, C_5^{smA}, Δ_1, and Δ_2 may be negative.

In the case when the wave vector is almost parallel to the layer normal, $q_\perp/q_z \ll \sqrt{C_5/C_3} \ll 1$, the bulk modulus dominates the fluctuation spectrum:

$$\langle |v(\boldsymbol{q})|^2 \rangle_z \approx V k_B T \frac{1 + (C_3/\Lambda) q_z^2}{C_3 q_z^2}$$

$$\to \frac{V k_B T}{C_3 q_z^2} \quad \text{at} \quad |\boldsymbol{q}| \approx q_z \ll \sqrt{\Lambda/C_3} \tag{30}$$

$$\to \frac{V k_B T}{\Lambda} = \text{const} \quad \text{at} \quad q_z \gg \sqrt{\Lambda/C_3}$$

$$\text{(still very small: } q_z \ll q_0). \tag{31}$$

The regime (30) occurs inside the narrow cone of wave vector directions, given by the condition $\theta \simeq \sqrt{C_5/C_3}$. For a typical elastomer this amounts to $\theta \ll 0.6°$, or even less when the smectic order is weak and $C_5^{\text{smA}} \sim \psi^2$. This essentially means pure compression modes along the layer normal.

The border between the bulk compressibility response to a longitudinal distortion and the, unusual in this context, "masslike" response (31) occurs at $q_z^* \sim \sqrt{\Lambda/C_3}$ $\sim [100R_0]^{-1}$. In the case of weak smectic order $q_z^* \sim \psi$ and,

therefore, both types of behavior can be readily accessed by a detailed experiment on layer compression extension.

Physical reasons for having the effective smectic-A elastic energy (28) proportional to an overall square power $\sim q^2$ are quite transparent and follow directly from the main feature of smectic order in a rubbery network—the relative translations coupling (9). In a liquid smectic, only layer curvature $\nabla_\perp^2 u$ is elastically penalized. When there is an underlying elastic network, coupled to the layer displacement, the usual smectic degeneracy with respect to uniform layer rotations $\nabla_\perp u$ is lost and we obtain the solidlike elastic energy, Eq. (28). Naturally, the renormalization is determined solely by rubber-elastic parameters: the shear modulus C_5 and coupling constants Δ. The special case is the longitudinal layer deformation of an incompressible smectic elastomer, when the system becomes very rigid indeed, controlled by the bulk modulus effects.

Equations (29) and (30) also tell us that there is no longer a Landau-Peierls instability of smectic fluctuations. The logarithmic divergence of the correlation function $\langle u(0)u(\boldsymbol{r}) \rangle$ is suppressed by the network elasticity. Therefore the x-ray scattering on smectic layers will no longer be purely diffusive, but will take a usual form of Bragg peaks with a thermal Debye-Waller factor. Scattering intensity in reciprocal space will take the form

$$I(\boldsymbol{q}) = \int d^3 r \, e^{i\boldsymbol{q} \cdot \boldsymbol{r}} \langle \rho(0) \rho(\boldsymbol{r}) \rangle = \int d^3 r \, e^{i(\boldsymbol{q} - \boldsymbol{q}_0) \cdot \boldsymbol{r}} \mathcal{S}(\boldsymbol{r}) \tag{32}$$

for the first-order reflection peak in an ideally infinite sample

(so that no additional finite-size peak broadening occurs). In an ordinary smectic, one obtains from the logarithmic divergence (24) [24]. In contrast, in an ideal defect-free smectic elastomer the diffusive scattering is far less important. The primary effect in the structure factor is a Debye-Waller constant given by direct integration of Eqs. (29) and (30).

The x-ray scattering intensity (32) becomes modulated by the Debye-Waller factor

$$\sim \exp\left[-\frac{1}{2} \frac{4\pi^2}{d_0^2} \langle |u|^2 \rangle \right],$$

where the mean-square fluctuation of layers is given by Eqs. (34) and (35). For each consecutive n-order peak one obtains

$$I(\boldsymbol{q}) \simeq \sum_n \delta\left(q_z - \frac{2\pi n}{d_0} \right) e^{-(1/2)(4\pi^2 n^2)/d_0^2 \langle |u|^2 \rangle}. \quad (33)$$

Far from the smectic-nematic transition, when the layer compression constant is large, $B \gg C_5$, one obtains

$$\langle |u|^2 \rangle \approx \frac{k_B T}{d_0 \sqrt{C_5^* B}}, \quad (34)$$

where C_5^* is defined in Eq. (29).

The limiting case, $C_5^{\mathrm{eff}}/B \gg 1$, can be achieved in a highly nonsoft elastomer, where the condition that $C_5^{\mathrm{eff}} \sim |\psi|^2$ is not satisfied but the smectic layer compression B and the relative-rotation couplings, Δ_1 and Δ_2 (which are proportional to $b_\perp$) are still $\sim |\psi|^2$. Then, in a network with a relatively high degree of crosslinking, near the smectic phase-transition point where $B, \Delta_1, \Delta_2 \to 0$, the mean-square fluctuation becomes

$$\langle |u|^2 \rangle \sim \frac{k_B T}{\pi d_0 4 C_5}. \quad (35)$$

Qualitatively, neglecting all effects of potential softness, uniaxial anisotropy and layering, all rubber moduli $C_i \sim \mu = c_x k_B T$. We have then for the Debye-Waller factor $e^{-n^2 W}$ in Eq. (33): $W \simeq (4\pi^2/d_0^2)\sqrt{l/c_x} \sim (lR_0/d_0^2)$ (where l is a characteristic size of a mesogenic monomer). At $c_x \to 0$ (strictly, below the network percolation limit) the Debye-Waller exponent diverges and thus suppresses the Bragg peak in the x-ray scattering intensity. The usual smectic-A diffusive scattering would then prevail.

Precision x-ray scattering requires a very narrow dispersion of the incident beam $I(q)$ in order to resolve the line shape of a smectic diffraction peak (Fig. 7). This is usually achieved by multiple-Bragg reflection in the monochromator and the analyzer crystals. A study of long-range order in a monodomain, side-chain, polymer smectic-A system capable of forming an elastomer by photocrosslinking has been performed recently by Wong et al. [28]. The freely standing films of smectic-A polymer were aligned in a magnetic field. Good monodomain orientation has been achieved, with the layer mosaic not exceeding 2.5° for the elastomer and 4.1° for the uncrosslinked polymer. The measurements using triple-reflection channel-cut Si crystals have achieved an incident-beam dispersion of $\sim 1/q^{3.6}$, sufficiently narrow to

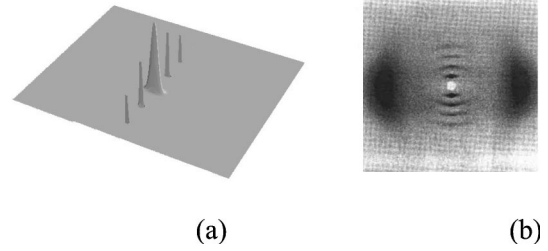(a)   (b)

FIG. 7. X-ray scattering of an aligned smectic elastomer: (a) a 3D projection of calculated scattering intensity, modulated by the Debye-Waller factor, Eq. (33); (b) the experimental image illustrates the high degree of orientational (nematic) order of mesogenic groups in the wide angles and the smectic (lamellar) order of layers with a number of multiple-order reflections in small angles. Image courtesy of R. Zentel.

resolve the difference between Bragg and Caille diffraction. The results produced a line shape for a smectic elastomer $I(q_z) \sim 1/q^{2.4}$ in a broad range of wave vectors down to the resolution limit of several inverse micrometers. In contrast, the same polymer material not crosslinked into the network, under the same conditions, shows the intensity profile $I(q_z) \sim 1/q^{1.85}$. As expected, this is somewhat less than the theoretical limit of $1/q^2$ for the Landau-Peierls quasi-long-range order, cf. Eq. (25).

Equation (33) describes the reduction in each consecutive Bragg peak intensity arising from thermal fluctuations controlled by the effective Hamiltonian (28). In real smectic elastomers, there are quenched random undulations of the smectic layers that result from the random nature of the crosslinking of the underlying network. These random undulations would lead to further reductions in Bragg peak intensity, but will not destroy the true long-range order in the periodic one-dimensional lamellar lattice. Quenched random distortions will also lead to additional diffuse scattering and the corresponding broadening of Bragg peaks.

V. CONCLUSIONS

We modeled the behavior of a smectic-A elastomer using a continuum expansion of the free energy in the small deformation limit. Interesting properties of this system, an elastic medium with a periodic layer microstructure, arise from the interplay between the two degrees of freedom, namely, the local displacement of the elastic matrix, and that of the smectic layers. Our results may thus be broken down into two groups. The first group details the effect of the smectic degrees of freedom on the macroscopic elastic properties of the system, namely, the elastic response and the moduli, summarized by the uniaxial Eq. (2) and the constants (21). The second group of results, in Sec. IV, describes the effects of the elastic matrix on the fluctuations of the smectic layers and, ultimately, on the state of lamellar order.

We determined the change in the elastic moduli due to the liquid-crystalline degrees of freedom by integrating out the fluctuations of the director and of the layer displacements. We also examined these changes using particular values of material constants derived from a molecular model for the underlying nematic elastomer system [1]. We found, unsurprisingly, that the presence of smectic layers destroys the

conditions required for soft nematic rubber elasticity. The effect of the renormalization of elastic moduli was negligible in the case of the bulk modulus but substantial—increasing them by an order of magnitude—in the case of two of the shear moduli C_1, C_2. The third shear modulus C_4 was unchanged leading to a large effective anisotropy in the average macroscopic elastic properties. This explains the large anisotropy found in the response moduli measured by Nishikawa and Finkelmann [21,22].

We determined the damping effect of the rubber-elastic matrix on the fluctuations of the smectic layers, improving the initial description given in Ref. [10]. In ordinary smectics, fluctuations only permit the existence of a quasi-long-range order in a one-dimensionally periodic layer stack. The elastic matrix, in which such layers are embedded in our case, was found to suppress these fluctuations, resulting in true long-range order being established. Precision x-ray diffraction experiments confirm this observation in real smectic-A elastomers, exhibiting many visible orders of Bragg peaks. The Debye-Waller factors, determining the attenuation of consecutive Bragg peaks, are calculated in two limiting cases: well within the smectic phase, and in the case of a highly nonsoft material near the nematic-smectic-A phase transition.

In conclusion, one should point out that an elastomeric material should allow large deformations to be sustainable. The present paper is confined to the limit of small strains and only describes the near-equilibrium response of the material. However, as in classical rubbers and solid crystals, one could make conjectures about the behavior at larger deformations. For certain strains (extensions or shears) in the layer plane there is no significant change due to the presence of lamellar order and a normal rubber-elastic response is expected to persist. Other deformations, such as an extension along the layer normal, are strongly affected by smectic density modulation and the high-modulus linear response predicted in this paper cannot exist for a large range of strains expected of a rubber. The Helfrich-Hurault instability occurs in the nonlinear regime and the layer system buckles in a periodic fashion, thus providing a lower-energy route to accommodate the strain $\tilde{\varepsilon}_{zz}$.

ACKNOWLEDGMENTS

APPENDIX A: EFFECTIVE ELASTIC MODULI $\mu_\parallel$ AND $\mu_\perp$

Consider two cases when a uniform extension is applied to a sample of monodomain smectic rubber, Fig. 6, in the two orthogonal principal orientations of layers. In this paper we only consider the infinitesimally small strains so that no effects of director or layer rotations are to be considered in the chosen orientations. Both geometries prevent macroscopic shear strains and the only relevant components of $\tilde{\varepsilon}_{\alpha\beta}$ are

$$\begin{pmatrix} \varepsilon_{xx} - \frac{1}{3}\mathrm{Tr}[\underline{\underline{\varepsilon}}] & 0 & 0 \\ 0 & \varepsilon_{yy} - \frac{1}{3}\mathrm{Tr}[\underline{\underline{\varepsilon}}] & 0 \\ 0 & 0 & \varepsilon_{zz} - \frac{1}{3}\mathrm{Tr}[\underline{\underline{\varepsilon}}] \end{pmatrix}$$

(with $\mathrm{Tr}[\underline{\underline{\varepsilon}}] = \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}$). We continue using a convention that the undistorted layer normal $\mathbf{k} = \mathbf{n}_0$ is along the z axis. The effective elastic energy, e.g., Eq. (2), is explicitly written in terms of the components of strain:

$$\begin{aligned} F_{\mathrm{elastic}} = & C_1(\tfrac{2}{3}\varepsilon_{zz} - \tfrac{1}{3}\varepsilon_{xx} - \tfrac{1}{3}\varepsilon_{yy})^2 + 2C_2(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}) \\ & \times (\tfrac{2}{3}\varepsilon_{zz} - \tfrac{1}{3}\varepsilon_{xx} - \tfrac{1}{3}\varepsilon_{yy}) + C_3(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz})^2 \\ & + 2C_4[(\tfrac{2}{3}\varepsilon_{xx} - \tfrac{1}{3}\varepsilon_{yy} - \tfrac{1}{3}\varepsilon_{zz})^2 \\ & + (\tfrac{2}{3}\varepsilon_{yy} - \tfrac{1}{3}\varepsilon_{xx} - \tfrac{1}{3}\varepsilon_{zz})^2], \end{aligned} \tag{A1}$$

where all moduli are taking their renormalized, effective values, Eq. (21).

In the case shown in Fig. 6(a), in-plane stretching, the strain $\varepsilon_{xx} \equiv \varepsilon$ is imposed. Two other components are obtained by minimization of the energy (A1). Neglecting terms proportional to μ/C_3, i.e., assuming full incompressibility, we have

$$\varepsilon_{yy} \approx -\frac{C_1}{C_1 + 2C_4}\varepsilon; \quad \varepsilon_{zz} \approx -\frac{2C_4}{C_1 + 2C_4}\varepsilon; \tag{A2}$$

$$\varepsilon_{yy} \to -\varepsilon; \quad \varepsilon_{zz} \to 0 \quad \text{at } C_1 \gg C_4$$

as illustrated in Fig. 6(a). At these optimal values of volume-conserving strains, the rise in elastic energy in response to the imposed strain ε is given by

$$F^* \approx 4\frac{C_4(C_1 + C_4)}{C_1 + 2C_4}\varepsilon^2$$

and, thus, the measured modulus

$$\mu_\perp = \frac{8C_4(C_1 + C_4)}{C_1 + 2C_4} \to 8C_4 \sim 4c_x k_B T.$$

In the case shown in Fig. 6(b), stretching along the layer normal z, the strain $\varepsilon_{zz} \equiv \varepsilon$ is imposed. Minimization with respect to two other components of strain gives

$$\varepsilon_{xx} \approx -\tfrac{1}{2}\varepsilon; \quad \varepsilon_{yy} \approx -\tfrac{1}{2}\varepsilon, \tag{A3}$$

the expected symmetric transverse contraction, as one finds in any isotropic incompressible material, see Fig. 6(b). The energy response to the imposed ε is now

$$F^* \approx (C_1 + C_4)\varepsilon^2$$

and the effective longitudinal modulus

$$\mu_\parallel = 2(C_1 + C_4) \to 2C_1 \sim B,$$

the smectic layer compression constant.

APPENDIX B: INTEGRATING OUT RUBBER-ELASTIC PHONONS

The Fourier transform of the free-energy density (14), which depends on both $\boldsymbol{v}(\boldsymbol{q})$ and $u(\boldsymbol{q})$, can be arranged as a quadratic form, Eq. (26), where the matrix elements are given by

$$\boldsymbol{v_q}=\begin{pmatrix} v_{\boldsymbol{q}z} \\ v_{\boldsymbol{q}\perp} \\ v_{\boldsymbol{q}t} \end{pmatrix}, \quad \boldsymbol{\Gamma}=\begin{pmatrix} \Lambda+\frac{1}{8}(\Delta_1+2\Delta_2)q_\perp^2 \\ -\frac{1}{8}(\Delta_1-2\Delta_2)q_zq_\perp \\ 0 \end{pmatrix}, \quad (B1)$$

$$G_{zz}\approx 2\Lambda+C_3q_z^2+\tfrac{1}{4}(8C_5+\Delta_1+2\Delta_2)q_z^2,$$

$$G_{\perp\perp}\approx C_3q_\perp^2+\tfrac{1}{4}(8C_5+\Delta_1-2\Delta_2)q_z^2$$

$$G_{tt}=2C_4q_\perp^2+\tfrac{1}{4}(8C_5+\Delta_1-2\Delta_2)q_z^2,$$

$$G_{\perp z}=G_{z\perp}\approx C_3q_zq_\perp ,$$

$$G_{\perp t}=G_{t\perp}=G_{zt}=G_{tz}=0, \quad (B2)$$

where the similar terms were neglected when appearing next to the bulk modulus C_3 (assuming, as always, $C_5/C_3\ll 1$) and the shear modulus C_5^{smA} is already renormalized by nem-atic director fluctuation modes. The coefficient penalizing the ''bare'' layer fluctuations $u(\boldsymbol{q})$ in Eq. (26) is given by

$$\mathcal{M}=2\Lambda+Bq_z^2+\Delta_1q_\perp^2+\tilde{K}q_\perp^4 \quad (B3)$$

(with $\tilde{K}=[b_\perp^2/(b_\perp+D_1)^2]K_1$). However, one expects it to change significantly when the rubber-elastic $\boldsymbol{v}(\boldsymbol{q})$ modes are integrated out.

The further calculation is straightforward and was already performed on other occasions: minimizing the quadratic form (26) we obtain the optimal modes of network deforma-tions, e.g., here $\boldsymbol{v_q}=2(\underline{\underline{G}}^{-1}\cdot\boldsymbol{\Gamma})u_q$ and the minimal (effec-tive) free-energy density becomes

$$F^{\mathrm{eff}}=\frac{1}{2}\left[\mathcal{M}(\boldsymbol{q})-4\frac{G_{zz}\Gamma_\perp^2-2G_{z\perp}\Gamma_z\Gamma_\perp+G_{\perp\perp}\Gamma_z^2}{G_{zz}G_{\perp\perp}-G_{z\perp}^2}\right]|u_q|^2.$$

The full expression, with matrix elements explicitly put in, is tedious but there are possible simplifying approximations due to the large bulk modulus (as always, neglecting terms of order C_5/C_3) and the constraint of small wave vectors (ex-plicitly estimated as $q\ll\sqrt{\Lambda/\mu}\sim 1/R_0$, the network span). After these are implemented, we have the effective energy density

$$F^{\mathrm{eff}}\approx\frac{1}{2}\left[\frac{8C_5^{\mathrm{eff}}q_z^4+(8C_5-3\Delta_1-\Delta_2)q_\perp^4-2(2\Delta_1-\Delta_2)q_z^2q_\perp^2}{4q_\perp^2+\left(\dfrac{4C_5^{\mathrm{eff}}}{C_3}\right)q_z^2+\left(\dfrac{4C_5^{\mathrm{eff}}}{\Lambda}\right)q_z^4}+Bq_z^2\right]|u_q|^2, \quad (B4)$$

where

$$C_5^{\mathrm{eff}}=C_5^{\mathrm{smA}}+\tfrac{1}{8}(\Delta_1-2\Delta_2),$$

cf. Eq. (21).

[1] M. Warner and E. M. Terentjev, Prog. Polym. Sci. **21**, 853 (1996).

[2] P. D. Olmsted, J. Phys. II **4**, 2215 (1994).

[3] F. S. Bates, Science **251**, 898 (1991).

[4] C. C. Honeker and E. L. Thomas, Chem. Mater. **8**, 1702 (1996).

[5] P. Fischer and H. Finkelmann, Prog. Colloid Polym. Sci. **111**, 127 (1998).

[6] B. Hahn, J. H. Wendorff, M. Portugall, and H. Ringsdorf, Colloid Polym. Sci. **251**, 875 (1981).

[7] V. P. Shibaev, S. G. Kostromin, and N. A. Plate, Eur. Polym. J. **18**, 651 (1982).

[8] P. D. Olmsted and E. M. Terentjev, Phys. Rev. E **53**, 2444 (1996).

[9] E. Nishikawa, H. Finkelmann, and H. R. Brand, Macromol. Rapid Commun. **19**, 181 (1998).

[10] E. M. Terentjev, M. Warner, and T. C. Lubensky, Europhys. Lett. **30**, 343 (1995).

[11] P. G. de Gennes, in *Liquid Crystals of One and Two-Dimensional Order*, edited by W. Helfrich and G. Heppke (Springer-Verlag, Berlin, 1980), p. 231.

[12] L. D. Landau and E. M. Lifshitz, *Theory of Elasticity*, 3rd ed. (Pergamon, Oxford, 1986).

[13] P. G. de Gennes and J. Prost, *Physics of Liquid Crystals* (Clarendon, Oxford, 1993).

[14] T. C. Lubensky, J. Chim. Phys. **80**, 31 (1983).

[15] S. A. Pikin, *Structural Transformations in Liquid Crystals* (Gordon and Breach, New York, 1991).

[16] W. Helfrich, Z. Naturforsch. A **33**, 305 (1978).

[17] E. Gebhard and R. Zentel, Macromol. Rapid Commun. **19**, 341 (1998).

[18] T. C. Lubensky, E. M. Terentjev, and M. Warner, J. Phys. II **4**, 1457 (1994).

[19] J. Weilepp and H. R. Brand, Macromol. Theory Simul. **7**, 91 (1998).

[20] D. J. Read, R. A. Duckett, J. Sweeney, and T. C. B. McLeish, J. Phys. D **32**, 2087 (1999).

[21] E. Nishikawa and H. Finkelmann, Macromol. Chem. Phys. **198**, 2531 (1997).

[22] E. Nishikawa and H. Finkelmann, Macromol. Chem. Phys. **200**, 312 (1999).

[23] B. D. Cullity, *Elements of X-ray Diffraction* (Addison-Wesley, Reading, MA, 1978).

[24] A. Caille, C. R. Acad. Sci. B **294**, 891 (1972).

[25] J. Als-Nielsen, J. D. Litster, R. J. Birgeneau, M. Kaplan, and C. R. Safinya, Phys. Rev. B **22**, 312 (1980).

[26] C. R. Safinya, D. Roux, G. S. Smith, S. K. Sinha, P. Dimon, N. A. Clark, and A. M. Bellocq, Phys. Rev. Lett. **57**, 2718 (1986).

[27] W. G. Bouwman and W. H. de Jeu, Phys. Rev. Lett. **68**, 800 (1992).

[28] G. C. L. Wong, W. H. de Jeu, H. Shao, K. S. Liang, and R. Zentel, Nature (London) **389**, 576 (1997).