Quenched random disorder and X-ray scattering in smectic elastomers

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In this work we examine layer fluctuations in a smectic elastomer with quenched random disorder induced by crosslinks. The system is analyzed in a continuum model and crosslinks are introduced as a random field in a microscopic picture. In the case of small deformations and replica symmetry the intensity profile for x-ray scattering along the layer normal was determined for layer displacements smaller than the layer separation. In this regime it is predicted that for large enough crosslink densities the first-order diffraction pattern of the solid assumes a Lorentzian form showing a decay of short-range order over a length scale of 20 nm. Crosslinks are observed to disorder the system by decreasing the correlation length, which we show not to be a consequence of the random field. The coupling to random crosslinks is predicted to retard the decrease of the correlation length and hence found to stabilize the 1-D periodic layer structure against thermal fluctuations. The dependence of the correlation length on the crosslink density leads us to propose an estimate for the percolation limit of a smectic elastomer network.

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INTRODUCTION

Smectic elastomers are subject of ongoing research activity, as they offer intriguing challenges for the experimentalist as well as the theorist. The remarkable properties of these materials are a direct consequence of their composition: mesogenic molecules are attached to a polymer backbone leading to both liquid crystalline and rubber-elastic qualities [1]. Moreover, the polymer backbones are crosslinked at random positions giving rise to two opposing effects: On the one hand crosslinks pin the smectic layer to the underlying elastic matrix which in turn suppresses layer bending fluctuations. On the other hand, crosslinks represent a quenched random field of defects that might disturb the smectic layers if there is a potential energy preference for these crosslink to be linked with the layers. Hence the role of crosslinks for the 1-dimensional translational order in smectic systems is a subject of an ongoing debate.

It is well established that smectic liquids display the Landau-Peierls instability. Thermal fluctuations cause the correlations of smectic layer fluctuations to diverge logarithmically leading to the quasi-long-range order [2, 3]. The resulting intensity signature in X-ray scattering experiments was predicted by Caillé [4] and was confirmed experimentally in classical experiments [5, 6]. The traditional periodic Bragg peaks reduce to a singular diffuse scattering peak with algebraically decaying tails.

In smectic elastomers the lamellar phase interacts with the underlying elastic matrix through crosslinks [7, 8]. Relative displacements of layers and the elastic medium are penalized, pinning layers together and correspondingly stabilizing the 1-D periodic structure. The resulting long-range order has been described theoretically [9, 10] and observed by Wong *et al.* [11].

Crosslinks can also be a source of disordering. In the process of crosslinking the elastic matrix couples to the smectic layers and can perturb these, thus adding quenched defects to the system. This random field of defects is suspected to affect smectic order negatively [12]. In a recent X-ray study of smectic elastomers Obraztsov *et al.* [13] showed both effects attributed to crosslinks: Whereas crosslinks initially improve translational order a further increase in crosslink concentration broadens the quasi-Bragg peaks corresponding to growing disorder. Besides, the characteristic quasi-long range order was observed up to high crosslink densities.

The presence of crosslinks also manifests itself in other properties of smA-elastomers: The mechanical response of these materials upon the application of stress perpendicular and parallel to the layers has been extensively examined both experimentally and theoretically. In most cases the elastic modulus in the direction parallel to the layer normal is much larger than the modulus in the direction parallel to the layers while in-plane fluidity is maintained [14]. If strained excessively the monodomain structure breaks down in favor of a zig-zag array of rotated layers and areas with nematic-like order [15]. A theoretical investigation using a microscopic picture based on a corrugated potential for crosslinks [8] was successful in confirming the experimental findings. This form of a corrugated potential for crosslinks will also be employed in the present work.

In smectic systems other than elastomers, disorder has been known to have drastic effects. Quenched disorder due to confinement of smectic liquid crystals in the random environment of an aerogel was observed to destroy the smectic translational ordering and only allow short-range correlations [16]. This effect is predicted to persist even for arbitrarily weak quenched disorder [17, 18].

All these findings motivate us to theoretically examine the importance of randomly distributed crosslinks for the translational order in smectic elastomers. Hence, in this paper we will develop a theoretical description of uniax-

ial monodomain smectic elastomers with a random field coupling. In the development of a continuum theory for smectic elastomers we will follow Osborne *et al.* [10], and introduce the random field induced by the crosslinks as an additional coupling to that theory, where crosslink points are confined in a corrugated potential. In particular, we will be interested in the consequences of random crosslinks for layer displacement fluctuations and the resulting behavior in X-ray diffraction experiments. At the end we will compare our results to experimentally observed phenomena.

In describing our model, as well as analyzing experimental results, it is important to distinguish different ways a smectic elastomer can be formed. Figure 1 illustrates three possible ways: In panel A we show how a well-formed smectic liquid crystal, aligned with the help of external fields or surfaces, can be crosslinked to preserve the layer structure. This system corresponds to theoretical description of [9, 10] and some of the experiments of [11, 14]. In panel B we assume that a uniaxially aligned (monodomain) nematic elastomer is established by first aligning and then crosslinking the network [19]; cooling the system down into the smectic A phase results in a system that preserves the uniaxial alignment but has frustrated layers due to random crosslink positioning. This is the system we study in this paper, and we believe this is the preparation protocol of Obraztsov *et al.* [13]. Finally, panel C shows a different scenario when the crosslinked elastomeric network is established in the isotropic phase (either above the nematic-isotropic transition, or when the smectic phase appears directly below isotropic). In this case we expect a strongly misaligned polydomain state in which both the layer structure and the nematic director would only have short-range correlations. Nematic polydomain systems are relatively well understood, both theoretically and experimentally [20, 21], while at present there is no theory to describe the equilibrium structure of polydomain smectic elastomers (apart from an extensive discussion of stress-induced regular domain patterns [8] and the elastic softness during domain alignment by external stress [22]).

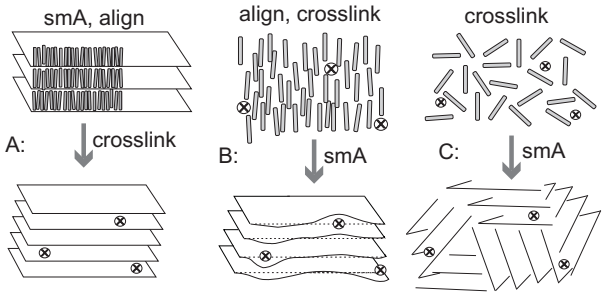

FIG. 1: Three ways of obtaining smectic elastomers, in decreasing order of resulting alignment. Procedure A results in a true monodomain smectic elastomer. Following the method B one obtains a uniaxially aligned elastomer with layer frustration, while the procedure C leads to a true polydomain smectic elastomer.

THE MODEL

Continuum description

We will base the model of a monodomain uniaxial smectic-A elastomer on a nematic elastomer that underwent the smectic-nematic transition and exhibits the smectic-A phase. In this process we will allow the nematic degrees of freedom to establish equilibrium, which mathematically corresponds to integrating out the nematic director fluctuations. The macroscopic properties of the material will be that of a lamellar system regardless of how the lamellar phase was reached. In addition, we restrict our examination to the uniaxial case (scenario B in Fig. 1) as these materials were studied in recent experiments [13].

Smectic order is characterized by the order parameter $|\psi(\mathbf{r})|$ which is allowed values between zero and one, corresponding to no smectic order and the perfect 1-dimensional order, respectively. We will only be interested in the smectic phase of the system as we are concerned with the correlation of smectic layers in the material and their displacement fluctuations. Therefore, we take the system to be far from the nematic-smectic transition by working well below the critical point T_{NA}. Consequently, the smectic order parameter can be taken as constant and uniform with a value of $|\psi(\mathbf{r})| = 1$.

We begin our description of liquid crystal elastomer by considering the relevant contributions to the continuum free energy density: this will include terms for the ordinary nematic, the smectic, and the elastomer. As we are only interested in the smectic phase, the nematic director fluctuations are integrated out as shown elsewhere [10]. The resulting smectic elastomer has two relevant degrees of freedom, the relative displacement fields of the layers $u(\mathbf{r})$ and of the elastic matrix $\mathbf{v}(\mathbf{r})$. Consequently, contributions to the effective free energy of the smectic elastomer either depend on one of the two displacement fields or consist of an interaction between the two:

(i) Deformations of layers of the smectic-A phase contribute to the energy density through a term F_{smA}.

(ii) The elastic response of a uniaxial material leads to an energy density term F_{el}.

(iii) Relative translations and rotations between the layers and the underlying elastic matrix are summarized in a coupling term F_c.

Bringing these results together one obtains the effective energy density $F_{smEl} = F_{smA} + F_{el} + F_c$. It was shown that in reciprocal space this expression can be ar-

ranged as a quadratic form [10]:

$$F_{smEl} = \frac{1}{2}\mathbf{v_q}\cdot\underline{\underline{\mathbf{G}}}(\mathbf{q})\cdot\mathbf{v_{-q}} + \frac{1}{2}\mathcal{M}(\mathbf{q})u_{\mathbf{q}}u_{-\mathbf{q}} - \mathbf{\Gamma}(\mathbf{q})\cdot[\mathbf{v_q}u_{-\mathbf{q}} + \mathbf{v_{-q}}u_{\mathbf{q}}]\ , \quad (1)$$

where the values of matrix coefficients $\mathbf{G}, \mathcal{M}$ and $\mathbf{\Gamma}$ are rather cumbersome and are explicitly given in [1, 10]. To obtain the full free energy density of the system the random field coupling now has to be added to the expression above.

Random Field Coupling

The coupling to the random field is introduced as an interaction pinning the layers to randomly distributed crosslinks [12]. The effect of crosslinks on the smectic phase is modelled by a corrugated potential which penalizes deviations of crosslinks from the local layer positions. In the case $|\psi(\mathbf{r})| = 1$ the potential takes the form

$$F_{RF} = \gamma\int \mathrm{d}^3\mathbf{r}\ c(\mathbf{r})\ \cos\left(q_0\left[z - u(\mathbf{r}) + v_z(\mathbf{r})\right]\right) \quad (2)$$

where γ is the interaction strength and $c(\mathbf{r})$ the crosslink concentration. In a continuum theory the crosslink concentration is a random function with a Gaussian probability distribution derived in [28]:

$$P\left[c\right] \propto \exp\left(-\int \mathrm{d}^3\mathbf{r}\frac{\left(c\left(\mathbf{r}\right)-c_0\right)^2}{2c_0}\right), \quad (3)$$

where c_0 is the mean number of crosslinks per unit volume is also the standard deviation.

Replica Hamiltonian

Adding all contributions to the free energy we can write the partition function for a smectic elastomer coupled to a random field as

$$\mathcal{Z} = \int \mathcal{D}u\mathcal{D}\mathbf{v}\ \exp\left(-\beta\left[F_{RF} + \int \mathrm{d}^3\mathbf{r}F_{smEl}\right]\right). \quad (4)$$

Physical quantities are calculated as the average over the disorder associated with the crosslinks. These disorder averages can be overcome using the replica trick [23], so in the case of the effective free energy of the system:

$$\beta F = -\left\langle \ln \mathcal{Z}\right\rangle_P = \lim_{n\to 0}\frac{1-\left\langle \mathcal{Z}^n\right\rangle_P}{n}, \quad (5)$$

with $\beta = 1/k_BT$. The disorder average over the n replicas of the system can be performed analytically . Since F_{RF} is the only term that depends on the crosslink concentration, the disorder average will only affect this term and couple different replicas together into the term F_{repl}. After coarse-graining the system by averaging over the period of the smectic modulation q_0^{-1} we find:

$$F_{repl} = -\lambda\sum_{a,b=1}^{n}\int \mathrm{d}^3\mathbf{r}\ \cos\left(q_0\left[u^a - u^b - v_z^a + v_z^b\right]\right), \quad (6)$$

where the effective coupling strength is $\lambda = c_0\beta\gamma^2/2$. The full replica Hamiltonian as appearing in the expression for the replicated partition function is then given by

$$H_{rep} = \int \mathrm{d}^3\mathbf{r}\Big(\sum_{a=1}^{n}\left[F_{smA}^a + F_{el}^a + F_c^a\right] - \lambda\sum_{a,b=1}^{n}\cos\left(q_0\left[u^a - u^b - v_z^a + v_z^b\right]\right)\Big). \quad (7)$$

The next step in our calculation is to integrate out the elastic matrix fluctuations $\mathbf{v}$ to obtain an effective free energy density that only depends on the layer displacements u. From this expression we will be able to derive the mean-square layer fluctuations.

Integrating out elastic phonons

Averaging over quenched random disorder left us with an energy term that couples different replicas together in the replica Hamiltonian. Strictly, the cosine in its expression renders the partition function a non-Gaussian integral and makes its evaluation analytically very hard (see [24] for a detailed treatment of such a system in the context of Abrikosov flux latices in disordered superconductors, including the hierarchical replica symmetry breaking). Noting that the interaction contains translationally invariant terms of the form $[u^a(\mathbf{r}) - u^b(\mathbf{r})]$ and $[v_z^a(\mathbf{r}) - v_z^b(\mathbf{r})]$ we will make quick progress by assuming weak disorder, so that the cosine-function can be expanded to its leading quadratic order. This is a significant simplification, which will not allow us to address delicate problems of replica symmetry breaking. However, the advantage is that we can find the qualitative analytical answers to correlation functions in the relevant range – and our conclusions about the enhanced order will be consistent with assuming the differences $q_0[u^a - u^b]$ are small. Rewriting the expanded expression of F_{repl} in reciprocal space it can be combined with the remaining energy terms (1) leading to a quadratic form for the replica Hamiltonian

$$H_{rep} = V^2\int\frac{\mathrm{d}^3\mathbf{q}}{2\pi}\sum_{a,b=1}^{n}\big(\frac{1}{2}\mathbf{v}_{\mathbf{q}}^a\cdot\underline{\underline{\mathbf{G}}}^{ab}(\mathbf{q})\cdot\mathbf{v}_{-\mathbf{q}}^b - 2\mathbf{\Gamma}^{ab}(\mathbf{q})\cdot u_{\mathbf{q}}^a\mathbf{v}_{-\mathbf{q}}^b + \frac{1}{2}\mathcal{M}^{ab}(\mathbf{q})u_{\mathbf{q}}^a u_{-\mathbf{q}}^b\big) \quad (8)$$

where the random field coupling has been subsumed into the redefined matrix coefficients $\underline{\underline{\mathbf{G}}}^{ab}(\mathbf{q})$, $\mathbf{\Gamma}^{ab}(\mathbf{q})$ and $\mathcal{M}^{ab}(\mathbf{q})$.

The expression for the replicated partition function is now a Gaussian integral and can be performed analytically. When evaluating Gaussian integrals the method of steepest descent is mathematically equivalent to evaluating the integral exactly. Hence the integration over elastic matrix fluctuations $\mathbf{v}_{\mathbf{q}}^{a}$ can be done by minimizing the replica Hamiltonian with respect to the matrix fluctuations. Performing the minimization of the quadratic form we find the optimal fluctuation modes to be $\mathbf{v}_{\mathbf{q}}^{a} = 2\,\underline{\underline{\mathbf{G}}}^{-1\,ac}(\mathbf{q}) \cdot \mathbf{\Gamma}^{cb}(\mathbf{q})\; u_{\mathbf{q}}^{b}$.

Inserting the optimal modes into the replica Hamiltonian we arrive at an effective energy expression in terms of the smectic layer fluctuations alone:

$$F_{smA}^{\text{eff}} = \frac{V^2}{2} \int \frac{\mathrm{d}^3\mathbf{q}}{(2\pi)^3}\, \mathcal{M}_{\text{eff}}^{ab}(\mathbf{q})\, u_{\mathbf{q}}^{a} u_{-\mathbf{q}}^{b}, \tag{9}$$

with $\mathcal{M}_{\text{eff}}^{ab} = \Big[\mathcal{M}^{ab}(\mathbf{q}) - 4\mathbf{\Gamma}^{ac}(\mathbf{q}) \cdot \underline{\underline{\mathbf{G}}}^{-1\,cd}(\mathbf{q}) \cdot \mathbf{\Gamma}^{db}(\mathbf{q})\Big]$. From the expression above we will be able to determine fluctuations of layer displacements and examine the behavior of our system in x-ray scattering experiments.

Smectic layer fluctuations

As we are only interested in fluctuations of the smectic phase, the observable spectrum is known to be expressed by the diagonal term in the replica space [24, 25]: $\left\langle |u_{\mathbf{q}}|^2 \right\rangle = \left\langle u_{\mathbf{q}}^{a} u_{-\mathbf{q}}^{a} \right\rangle$. The full expression for $\left\langle |u_{\mathbf{q}}|^2 \right\rangle$ is rather tedious. However, we can employ simplifying approximations to focus on relevant physical consequences and present the results in a compact form. We regard the system as essentially incompressible such that the bulk modulus C_3 is taken to be very large compared to the other elastic moduli. Hence terms of order $C_5/C_3 \ll 1$ can be ignored. Another possibility to simplify our expression can be derived from the setup of scattering experiments. In X-ray scattering studies [13] the incident and scattered beam are close to the layer normal of the smectic, which results in the excitations of the material (the scattering vector $\mathbf{q}$) to be mainly along the layer normal. Consequently we take the wave vector components along the layer normal to dominate over components in the layer plane: $q_z \gg q_\perp$. In addition to this restriction we only consider wave vectors that are small (and the corresponding length scale large) in the sense that they obey $q \ll \sqrt{\Lambda/C}$, where C is a characteristic magnitude of the rubber shear modulus.

Applying these approximations we finally obtain the expression for the fluctuations of layer displacements:

$$\left\langle |u_{\mathbf{q}}|^2 \right\rangle \approx \frac{k_B T}{2V\Lambda} \left(\frac{1}{1 + \frac{B}{2\Lambda} q_z^2} \right) + \frac{c_0 q_0^2 \gamma^2}{4V\Lambda^2} \left(\frac{1}{1 + \frac{B}{2\Lambda} q_z^2} \right)^2 \tag{10}$$

The constant B in this expression is the layer compression modulus that also appears in the free energy density of a smectic liquid: $F_{smA} = \frac{1}{2}\left(B q_z^2 + K q_\perp^4\right)\, |u_{\mathbf{q}}|^2$.

RESULTS AND DISCUSSION

Importance of the random field

We obtained an expression for the mean-square layer displacements that consists of two contributions (10): the first term displays ordinary thermal fluctuations, modified by the coupling of smectic layers to the elastic matrix, whereas the second term represents the effect of the random field of crosslinks. The first term coincides with the expression that was obtained before by Osborne [10] and has the form of a Lorentzian with a characteristic length scale given by $\sqrt{B/2\Lambda}$. We now observe that the fluctuation term due to the random field has the form of the square of a Lorentzian with the same length scale $\sqrt{B/2\Lambda}$. This form already gives us hints about the relevance of the random field for the behavior of layer fluctuations. For relatively large wave numbers q_z this term behaves like ${q_z}^{-4}$ and will be dominated by the thermal fluctuations which only decrease like ${q_z}^{-2}$, in the way similar to the classical Larkin effect of quenched disorder in a lattice [26]. For small wave numbers q_z both the thermal and the random field term have a finite cutoff "mass". The relative magnitude of the random field is not negligible and we will hence assess its strength in comparison to the thermal part.

Note that the coupling constant Λ was analyzed on dimensional grounds [1] to be of the form:

$$\Lambda \approx \alpha c_0 \frac{k_B T}{R_0^2}\,, \tag{11}$$

where α is a non-dimensional coefficient of order unity and R_0 is the characteristic distance between two crosslinking points in the network. Using this estimate for Λ we can investigate the role of the random field contribution. For this term to dominate thermal fluctuations the coupling constant γ has to satisfy the condition

$$\gamma > k_B T \sqrt{\frac{d_0}{R_0}} \tag{12}$$

where d_0 is the smectic layer separation. As any crosslinking of physical significance for the material has to connect points that are separated by at least one smectic layer it can safely be assumed that $\frac{d_0}{R_0} < 1$ and, with

k_BT being the only energy scale in this system, γ easily meets the condition above. Therefore, we obtain the interesting result that the smectic layer fluctuations are dominated by the random-field term for small wavenumbers (i.e. for correlations at long length scale). This will have interesting consequences on translational order in smectic elastomers.

Given the linear dependence of Λ on the crosslink concentrations we note that both terms in the expression for the mean-square layer displacements (10) are inversely proportional to the crosslink density. This behaviour will be of importance when analyzing the properties of smectic elastomers in x-ray scattering experiments.

X-ray scattering

We will now proceed to examine the consequences of our theory for the intensity of X-rays scattered from the structured elastomer. In particular we will be interested to compare our predictions to the results of a recent study by Obraztsov et al. [13]. They investigated the influence of disorder induced by random crosslinks study on smectic elastomers. Quasi-Bragg peaks were identified and their lineshape accurately determined. For small crosslinking densities the central part of the peaks can be described by a Gaussian, however, upon increasing the crosslink density the peaks broaden and the Gaussian transforms into a Lorentzian lineshape. The tails of the quasi-Bragg peaks showed algebraic decay characteristic of quasi-long range order.

For an ideally infinite smectic material the intensity of the first-order reflection peak in reciprocal space is of the form

$$I(\mathbf{q}) \propto \int \mathrm{d}^3\mathbf{r}\; e^{i\mathbf{q}\cdot\mathbf{r}}\;\langle\rho(\mathbf{0})\rho(\mathbf{r})\rangle \propto \int \mathrm{d}^3\mathbf{r}\; e^{i(\mathbf{q}-\mathbf{q_0})\cdot\mathbf{r}}\;\mathcal{S}(\mathbf{r}) \tag{13}$$

with the structure factor $\mathcal{S}(\mathbf{r})$ is given by the average $\langle\exp\left(iq_0\left[u(\mathbf{r})-u(\mathbf{0})\right]\right)\rangle$. In the harmonic approximation the structure factor can be written in terms of a layer displacement correlation function, utilizing the basic property of Gaussian distributions:

$$\mathcal{S}(\mathbf{r}) = \exp\left(-\frac{q_0^2}{2}\left\langle\left[u(\mathbf{r})-u(\mathbf{0})\right]^2\right\rangle\right) \tag{14}$$

To proceed with the calculation of scattering intensity we recall the results of previous work on fluctuations in smectic elastomers. Our expression for layer displacement fluctuations coincides asymptotically with the result obtained by Osborne [10]. There it was concluded that fluctuations with the spectrum of this form in reciprocal space prevent the divergence of the mean-square fluctuations in real space:

$$\left\langle u^2\right\rangle \cong \frac{k_BT}{d_0\sqrt{2C_5^*B^*}} \tag{15}$$

Consequently, we can take the displacements of layers $u(\mathbf{r})$ to be small compared to the layer spacing $d_0 = 2\pi/q_0$. This is consistent with the Lindemann criterion [27] for crystalline lattices far from their melting point. In this limit the argument of the exponential in the expression for $\mathcal{S}(\mathbf{r})$ is taken to be sufficiently small to justify an expansion to first order: $\mathcal{S}(\mathbf{r}) \approx 1-\frac{1}{2}q_0^2\left\langle\left[u(\mathbf{r})-u(\mathbf{0})\right]^2\right\rangle$. The resulting intensity of the first-order X-ray diffraction peak consists of a broad lineshape superposed on a delta-functional Bragg-peak attenuated by a Debye-Waller-factor:

$$I(\mathbf{q}) \propto e^{-q_0^2\langle u^2\rangle}(2\pi)^3\delta^3(\mathbf{q}-\mathbf{q_0}) + q_0^2V\left\langle\left|u_{\mathbf{q}-\mathbf{q_0}}\right|^2\right\rangle \tag{16}$$

Let us examine the above result. The delta-function represents a true Bragg-peak showing the remnant long-range order in the system. The amplitude of the Bragg-peak corresponds to a first-order expansion of a Debye-Waller factor of the form $\propto \exp\left[-(4\pi^2/d_0^2)\left\langle u^2\right\rangle\right]$. In our approximation of small layer displacements $\left\langle u^2\right\rangle$ the amplitude of the Bragg-peak is close to its maximum value hinting on the presence of true long-range order in the system. This behavior is consistent with previous studies of smectic elastomers [9, 10].

The second term of expression (16) corresponding to the broad lineshape is entirely dictated by the mean-square displacement fluctuations in reciprocal space. To compare our results to experiment we will need to take the setup of X-ray studies into account. In experiments [13] the incident and scattered beams were closely aligned with the normal to the smectic phase, leading to the scattering vector components $q_z \gg q_\perp$. We already calculated an expression for $\left\langle\left|u_{\mathbf{q}-\mathbf{q_0}}\right|^2\right\rangle$ in this limit which we found to be of Lorentzian form (10):

$$I(\mathbf{q}) \propto \frac{k_BT}{2V\Lambda}\left(\frac{1}{1+\frac{B}{2\Lambda}(q_z-q_0)^2}\right) + \frac{c_0q_0^2\gamma^2}{4V\Lambda^2}\left(\frac{1}{1+\frac{B}{2\Lambda}(q_z-q_0)^2}\right)^2. \tag{17}$$

Several lessons can be learnt from this result. Thermal fluctuations display a Lorentzian intensity profile with a correlation length $\xi = \sqrt{B/2\Lambda}$ whereas the random field of crosslinks leads to the lineshape of the square of a Lorentzian characterized by the same length scale. This form allows us to analyze the quality of the short-range order exhibited in our system: The characteristic length displayed by this lineshape is a measure for the distance over which good translational order persists. Using previous estimates for the values of B and Λ in smectic elastomers [1] we obtain $\xi \approx 20$nm. Since the coupling parameter Λ is known to be proportional to the crosslink density c_0, this correlation length decreases with a growing number of crosslinks. Hence we demonstrated the

ability of crosslinks to impair translational order, but the precise emergence of this effect is somewhat unexpected: the decrease of the correlation length is also observed in the case of thermal fluctuations and is not purely an effect of the random field.

In addition, it can be observed that the lineshape caused by the random field of crosslinks is always narrower than the lineshape due to thermal fluctuations. The envelope for the intensity profile due to the random field decays faster than q^{-2} far away from the central peak. Such a behavior was observed by Wong [11], where the intensity was observed to decrease like $\sim q^{-2.4}$. We combine this finding with the above result regarding the relative strength of the random field fluctuations to arrive at the following surprising conclusion: the presence of random crosslinks in our system actually improves short-range translational order versus thermal fluctuations.

Finally, the dependence of the diffraction pattern on the crosslink concentration is examined. Layer fluctuation correlations (10) are found to be inversely proportional to the crosslink density which will determine the behavior of the Debye-Waller factor and the relative strength of various terms contributing to the scattering intensity. So the first two terms in the intensity profile (16) are of comparable strength if $q_0^2 \left\langle |u_{\mathbf{q}-\mathbf{q_0}}|^2 \right\rangle_{q_z \gg q_\perp} \sim 1$. Using the dependence of the layer fluctuation correlations on the crosslink density, the above condition can be rearranged as a constraint on the concentration of crosslinks. For the Lorentzian lineshape to contribute significantly to the diffraction pattern we require a crosslink number density of

$$c_0 \sim \frac{R_0^2}{d_0^2 V}. \tag{18}$$

For higher concentrations the Lorentzian lineshape is suppressed in favor of Bragg peaks, revealing true long-range order. On the other hand, on lowering the crosslink density the Debye-Waller factor attenuates the Bragg peaks and the intensity profile becomes increasingly Lorentzian-like indicating the presence of only short-range order. This emergence of a Lorentzian lineshape for high crosslink densities is in general agreement with experiment and was in particular highlighted recently [13]. When decreasing the crosslink concentration even further we leave the regime of small layer displacements and the diffraction pattern has to be determined from the full expression of the structure factor (14). Besides, our expression for the lineshape appears to be singular for the crosslink density approaching zero. In this case (c_0, C, $\Lambda \to 0$) our previous approximations break down and hence our result for scattering intensity becomes invalid. For the case of a vanishing crosslink density c_0 our system naturally returns to the smectic liquid whose intensity profile was obtained by Caillé [4].

Percolation limit

Obraztsov et al. [13] measured a broadening of first-order diffraction peaks upon increasing the concentration of crosslinks. In the case of X-rays scattered off an elastomer prepared with the stiff cross linker V8, the central parts of the peaks were well described by Lorentzians. For crosslink volume fractions of x =0.1, 0.125, and 0.15 the Lorentzians correspond to a correlation length of ξ = 53, 26, and 15 nm, respectively [13]. If expressed as a power law, the correlation length roughly depends on the volume fraction of crosslinks as $\xi \sim x^{-3}$, however tenuous this conclusion might be with so few points and the inevitable experimental error. Let us compare this relation to the correlation length obtained from our theory. Due to the dependence of the coupling parameter Λ on the number density of crosslinks c_0 (11), the relation between correlation length and crosslink number density is: $\xi = \sqrt{B/2\Lambda} \propto c_0^{-1/2}$.

As we expect the relation between the volume fraction of crosslinks and their number density to be roughly linear, $x \propto c_0$, we note that the predicted relation between correlation length and crosslink density is very different from the observed power law, however tentative: the measured correlation length drops off fast with increasing crosslink density whereas the predicted decrease is considerably weaker. This apparent discrepancy might be resolved by taking the percolation limit of an elastomer into account. This limit is the minimum concentration of crosslinks $c_{\min}$ needed to form an elastic network when synthesizing an elastomer. The elastic properties of the material should only depend on the excess of crosslinks over this minimum, that is, $\Lambda \propto (c_0 - c_{\min})$, leading to an amended expression for correlation length: $\xi \propto (c_0 - c_{\min})^{-1/2}$. We note that for crosslink concentrations close to the percolation limit c_{min} the changes in the correlation length can be much more drastic. A fit of this theory is shown in Fig. 2 leading to an estimate volume fraction of $x_{\min} \approx 0.09$ at percolation limit of elastic network. Considering the level of our approximations, as well as the somewhat ambiguous way the "crosslinking density" is quoted in experimental reports (volume-% vs. molar-%, possibly accounting for the double-bond on the crosslinking molecule), this is a very reasonable estimate of percolation threshold.

Real-space correlations

We want to find the real-space fluctuation correlations corresponding to the mean-square fluctuation in reciprocal space as given by Eq.(10). Hence excitations of the elastomer are again taken to be mainly along the smectic layer normal. The two terms of (10) are considered separately and integrated directly. The thermal contribu-

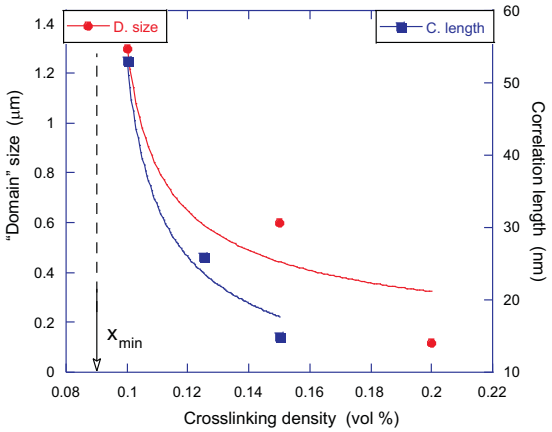

FIG. 2: Correlation length of "elastomer II" with stiff crosslink V8 and domain size of "elastomer II" with flexible crosslink V1 plotted against the volume fraction of crosslinks [13]. The solid lines represent the fit assuming a percolation limit of $x_{\min} \approx 0.09$.

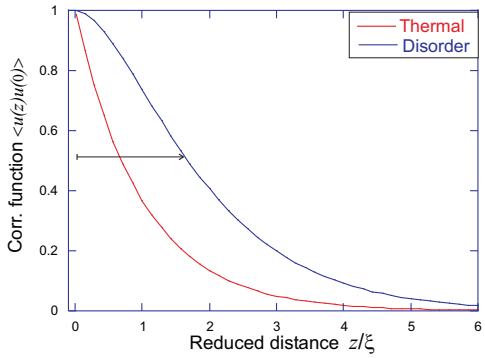

FIG. 3: Components of the real space correlation functions plotted against reduced distance along the layer normal, z/ξ: the thermal fluctuations (Lorentzian structure factor) and the quenched distortions due to crosslinks (square-Lorentzian), cf. Eq.(20). Both functions where normalized to 1 at $z = 0$ to allow for comparison.

tion to fluctuation correlations along the layer normal is the simple exponential (corresponding to the Lorantzian structure factor) with a decay length ξ:

$$\langle u(z)u(0)\rangle \sim \frac{k_B T}{a^2\sqrt{\Lambda B}}\, e^{-\sqrt{2\Lambda/B}|z|}, \qquad (19)$$

where a is the intra-layer distance between two mesogens, which is the short-distance cutoff in this system. In contrast, the random field of crosslinks leads to an expression:

$$\langle u(z)u(0)\rangle \sim \frac{c_0 q_0 \gamma^2}{a^2 \Lambda B}\left(\sqrt{\frac{2\Lambda}{B}} + |z|\right) e^{-\sqrt{2\Lambda/B}|z|}. \qquad (20)$$

The Landau-Peierls-divergence is removed, however, positional correlations now decay with the characteristic length scale $\xi = \sqrt{B/2\Lambda}$ showing the nominally short-range order. The quenched random field has the effect of retarding the exponential decay by the prefactor that depends linearly on z, effectively extending the range of correlations, as can be seen in Fig. 3. This is consistent with our observation that the introduction of randomly distributed crosslinks improves translational order. The slowdown of the exponential decay is only significant over a distance of a few correlation lengths hinting that the coupling to random crosslinks primarily enhances short-range order within the material.

One should point out that our theory was developed in the limit of small deformations and correspondingly breaks down for large wavenumbers q. In addition, scattering intensity profiles were derived for the case that layer displacements are small compared to the layer spacing, which in turn enforces a lower bound on the crosslink concentration (18). However, this requirement may be in conflict with another assumption made during the development of the theory. Crosslink densities were taken as small enough to maintain a replica-symmetric regime, rendering the theory less reliable for the case of large numbers of crosslinks. For a better description the domain of strong quenched disorder could be explored more rigorously in an approach based on replica symmetry breaking.

Yet, the work presented here shows consistence with experiment: As predicted, for high enough crosslink concentrations the central parts of the quasi-Bragg peaks measured by Obraztsov were well approximated by Lorentzians [13]. In contrast, our work is unable to account for the observation of algebraic decay of the tails of the peaks at large wavenumbers and the lineshape at low crosslink densities. A description of this behavior in elastomers remains a theoretical challenge.

Besides, intra-layer excitations of the smectic phase were largely ignored in this analysis owing to the setup of X-ray studies [13], which we have focused on, and the restriction to small layer displacements. A more complete theoretical approach should incorporate these excitations into the theoretical edifice leading to improved predictions both for fluctuation correlations and scattering lineshapes. In addition, our treatment is restricted to monodomain uniaxial elastomers, albeit real materials exhibit a range of layer normals within the material. A different theoretical approach is needed to properly describe this situation.

CONCLUSION

A monodomain uniaxial smectic-A elastomer was analyzed for small deformations in a continuum model and with the quenched random disorder introduced by coupling to a field of randomly distributed network crosslinks. The average over disorder was treated using the replica trick in a dilute regime of crosslinks, main-

taining the replica-symmetric regime.

We predicted the lineshape of the first-order peak for x-ray scattering normal to the smectic phase. For crosslink densities $c_0 > \frac{R_0^2}{d_0^2 V}$ a true Bragg peak modulated by a Debye-Waller factor is obtained asserting the presence of long-range order. This part of our theory confirms previous work on this subject [9, 10].

For crosslink densities $c_0 \sim \frac{R_0^2}{d_0^2 V}$ the x-ray intensity profile is of Lorentzian form exhibiting short-range ordering with a characteristic length $\xi = \sqrt{\frac{B}{2\Lambda}}$. This leads to exponentially decaying real-space fluctuation correlations (19) indicating good translational order over a distance $\xi \approx 20$nm. As the coupling constant Λ depends on the crosslinking density we demonstrate that the presence of crosslinks does introduce disorder even in the monodomain, well-aligned system of smectic layers. The correlation length depends on the crosslink concentration as $\xi \propto 1/\sqrt{c_0 - c_{\min}}$ causing the regions ('domains') of good translational order to shrink with a growing number of crosslinks. It should be appreciated that this effect of disordering is not a consequence of quenched random disorder introduced by the random field: the decrease of the correlation length is also observed in the purely thermal-fluctuation contribution, even though we expect in practice that the magnitude of fluctuations would be dominated by the quenched-disorder contribution to our main result, the Eq. (17).

This domination has important consequences: the predicted intensity profile due to the random field has the form of the square of a Lorentzian with the same characteristic length scale ξ. It is this form of a squared Lorentzian that retards the exponential decay of positional correlations and hence improves translational order (20) compared to the purely thermal case (19). Thus the presence of the random field of crosslinks, when they are established in a uniaxially aligned (nematic) system, stabilizes the 1-D translational smectic order against thermal fluctuations causing the size of domains of good translational order to exceed the correlation length ξ.

Further, our results have been compared to experiment: X-ray scattering peaks are predicted to broaden with increasing crosslink concentration which is qualitatively consistent with observations [13]. A quantitative comparison to experiment leads us to speculate about the percolation limit of the elastomers studied: analyzing the observed dependence of the correlation length on the crosslink concentration it is estimated that a volume fraction of 9% of crosslinks is needed to form an elastic network within these materials. This result is highly speculative and presented as a motivation for further investigation.

One should point out that our theory is far from offering a complete description of the behavior of smectic elastomers with random crosslinks: the remnant quasi-long range order as observed by Obraztsov [13] in the algebraic decay of the x-ray intensity profile is not accounted for in this work. In addition to that, intralayer excitations in the system were widely ignored and crosslink concentrations assumed to be small throughout. A further theoretical investigation of smectic elastomers should compensate for these shortcomings.

On the other hand, interesting contributions to the debate about the role of random crosslinks have been made. We were able to demonstrate both known tendencies of the behavior of crosslinks in smectic elastomers. So we found crosslinks to impair translational order by penalizing relative displacements between the layers and the elastic medium. Ironically, when introduced in the form of quenched random disorder, crosslinks have the counter-intuitive effect of stabilizing translational order against thermal fluctuations.

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