# Electronic supporting information

# Transient response and domain formation in electrically deforming liquid crystal networks

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In this ESI we discuss in detail the derivation of the theory we use in the main text. In Sec. I we motivate the formulation of the model free-energy functional, paying particular attention to how our boundary conditions differ from work we published previously [1]. In Sec. II we explain the model dynamics, and include a discussion on the implementation of the relaxation function  $\tau$  ( $z_0, t$ ) introduced in the main text. Finally, in Sec. III we describe the scaling procedure we use.

## I. EQUILIBRIUM THEORY

We describe the liquid crystal network in terms of two key order parameters: one characterising the orientational order of the mesogens and the other specifying the concomitant volume expansion. The former of these is the driving force in the model. Since only one species of mesogen responds appreciably to an applied electric field, the other being fully crosslinked into the network, we suffice by considering only the reorientations of pendant, dipolar mesogens against a background of immobile cross-linked mesogens. In a previous publication [2], we carried out molecular dynamics computer simulations indicating that, upon application of an electric field, the dipolar mesogens generally either (i) reorient to align with the electric field, perpendicular to the cross-linked mesogens, or they (ii) are hampered in their orientation due to the (excluded-volume) interactions with the crosslinked mesogens, remaining along their initial axis or orientation [2]. This motivates us to construct a two-population model in terms of the order parameter f [-], where  $0 \le f^2 \le 1$ is the fraction of electric-field-aligned dipolar mesogens. Note that we write  $f^2$ , rather than f, to ensure a consistent interpretation as a (positive) fraction.

The above suggests a competition between the electric field, quantified by the field strength H [J/m<sup>3</sup>][3], favouring reorientation of the dipolar mesogens along the electricfield axis on the one hand, and the (excluded-volume) interactions with the cross-linked mesogens, favouring the initial axis of orientation, on the other hand. We quantify the latter by a critical field strength  $H_*$  [J/m<sup>3</sup>], implying there is a threshold value for the electric field strength above which reorientation of the dipolar mesogens becomes energetically favourable. Such a critical field strength emerges naturally from a more elaborate derivation of the theory, as discussed in a previous publication [2], and can be shown to depend on the linear dimensions of the mesogens, their orientational order at the time of crosslinking and the crosslinking fraction of the network. Experiments suggest that to overcome this critical field strength, in practice an electric field of approximately  $4-5 \text{ V/}\mu\text{m}$  is required in the frequency range of 600-900 Hz [4]. The Gibbs free energy per unit *reference* volume can then be written as[5]

$$g_1 = \frac{1}{2} \left( H_* - H \right) f^2 + \frac{1}{4} B_f f^4, \tag{1}$$

where  $B_f$  [J/m<sup>3</sup>] denotes a bulk-modulus-like coefficient that tempers mesogen reorientation, as this induces local strains in the polymer matrix. Although such a term is not strictly required to bound the free energy from below, provided we enforce the condition  $0 \le f^2 \le 1$ post hoc, its inclusion ensures that a minimisation of Eq. (1) can produce intermediate order parameter values  $0 < f^2 < 1$ , representing alignment of a fraction of dipolar mesogens.

Following this, we introduce the volume-expansion order parameter  $\eta = (V - V_0) / V_0$  [-], with V and  $V_0$  the current and initial system volume, respectively. Expansion is driven by the mutually-excluded volume of the mesogens, meaning that an increased fraction of dipolar mesogens aligned with the electric field, and so perpendicular to the axis of orientation of the cross-linked mesogens, favours an increase in system volume. Neglecting, for now, the viscoelastic relaxation of the network (we shall return to this below when we discuss our model dynamics), and taking  $\xi$  [J/m<sup>3</sup>] as the coupling coefficient, we supplement Eq. (1) with

$$g_2 = -\xi \eta f^2 + \frac{1}{2} B_\eta \eta^2.$$
 (2)

The bulk-modulus-like term proportional to  $B_{\eta}$  [J/m<sup>3</sup>] is now formally required to keep the free energy bounded from below. We refrain from adding an explicit pressure-volume contribution, as the role of pressure can effectively be absorbed in model parameters (not shown).

The total Gibbs free energy follows by integrating  $g = g_1 + g_2$  over the initial volume of the system, a thin film extending from  $z_0 = 0$  to  $L_0$ , the initial thickness of the film, to yield [1]

$$\frac{G}{A} = \int_{0}^{L_{0}} \mathrm{d}z_{0} \left[ g + \frac{\kappa_{f}^{2}}{2\left(1 + \eta\left(z_{0}\right)\right)^{2}} \left(\frac{\partial f\left(z_{0}\right)}{\partial z_{0}}\right)^{2} + \frac{\kappa_{\eta}^{2}}{2\left(1 + \eta\left(z_{0}\right)\right)^{2}} \left(\frac{\partial \eta\left(z_{0}\right)}{\partial z_{0}}\right)^{2} \right], \quad (3)$$

with A the lateral area of the liquid crystal network. Here, the square-gradient contributions with the phenomenological coefficients  $\kappa_f \ [\sqrt{J/m}]$  and  $\kappa_\eta \ [\sqrt{J/m}]$  promote smooth spatial profiles of the corresponding order parameters. Strictly speaking, such coefficients derive from local interactions [6], and hence are not fully independent from other model parameters. Nevertheless, we shall treat them as free parameters for simplicity. The prefactor  $1/(1 + \eta (z_0))^2$  makes explicit the geometric significance of the volume-expansion order parameter,  $\eta (z_0)$ , in locally smearing out such spatial gradients.

The equilibrium state of the liquid crystal network is recovered by functionally minimising Eq. (3) with respect to the order parameters  $f(z_0)$  and  $\eta(z_0)$ , subject to the following boundary conditions. At the bottom of the film, all mesogens are clamped to the substrate, and so remain along their initial axis of orientation regardless of the applied electric field. Since a lack of reorientation in turn precludes local volume expansion, we impose  $f(0) = \eta(0) = 0$ .

At the top of the film, we model a diffuse interface of the liquid crystal network with the ambient medium. We assume that the density varies continuously across the interface, such that the volume-expansion order parameter  $\eta(z_0)$ , which is proportional to an inverse density, assumes its maximum value at  $z_0 = L_0$ . We compute this saturated expansion by minimising  $g_2$ , enforcing the restriction  $0 \leq f^2 \leq 1$ , which gives  $\eta(L_0) = \xi/B_{\eta}$ . For the population order parameter we demand  $\partial_{z_0} f(L_0) = 0$ , prohibiting order parameter flow through the top of the film. The diffuse interface influences  $f^2(z_0)$  through the model couplings.

This final boundary condition is slightly different from the one we used in our previous work [1], but turns out to be crucial to recovering three distinct time scales. After all, a Dirichlet boundary condition such as  $f(L_0) = 1$ , like we used in Ref. [1], would initialise the top with an already saturated response, leading to immediate permeation. Although this was sufficient for our aims in this prior publication, namely the study of permeation, such an initialisation is evidently ad hoc. The boundary condition we use in this paper does not suffer from this, as it presupposes no initial response in the absence of an electric field. Instead, this boundary condition prevents order parameter flow through the top of the film, beyond which the mesogen response has no physical meaning. Hence it is the more logical choice for the study of *transient* dynamics.

This concludes the discussion of our equilibrium theory. Below, in Sec. II, we explain how we extend this framework to also study the dynamical behaviour of the liquid crystal network.

### II. RELAXATIONAL DYNAMICS

To describe the temporal evolution of the order parameters, which we treat as nonconserved [7], the simplest form of dynamical equations describes relaxational dynamics, according to

$$\partial_t f = -\Gamma_f \frac{\delta G}{\delta f} + \theta_f,$$

$$\partial_t \eta = -\Gamma_\eta \frac{\delta G}{\delta \eta} + \theta_\eta - \gamma \ (\eta - \eta_0) \ \tau \left(z_0, t\right).$$
(4)

Here,  $\Gamma_f$  [m<sup>3</sup>/Js] and  $\Gamma_\eta$  [m<sup>3</sup>/Js] denote kinetic coefficients that encompass the dissipative processes through which the free energy may be lowered by variation of the relative order parameter. The Gaussian noise terms  $\theta_f$  [1/s] and  $\theta_\eta$  [1/s] ensure that the system eventually approaches the global minimum of the free energy, and that the fluctuation-dissipation theorem is satisfied [8]. In particular, the Gaussian noise terms enable the system to depart from its initial configuration, which is marginally stable.

The set of dynamical equations is complemented by a term reflecting the viscoelastic relaxation of the polymer network, which we neglected in the previous section. This term, proportional to the phenomenological coefficient  $\gamma$  [1/s<sup>2</sup>], guarantees that the volume-expansion order parameter profile,  $\eta$  ( $z_0$ , t), invariably relaxes back to its initial profile, i.e., the equilibrium profile it assumes in the absence of an electric field,  $\eta_0$  ( $z_0$ ), as a function of time t. This presupposes an enforced equilibrium of the model, imposed on top of the free energy functional of Eq. (3), and is informed by the experiments of Liu, Van der Kooij, and coworkers [4, 9, 10], and the molecular dynamics computer simulations we reported on in our previous work [2].

To achieve viscoelastic relaxation of the volume-expansion order parameter,  $\eta(z_0)$ , in Eq. (4) it is insufficient to simply write the relaxational term as  $-\gamma(\eta - \eta_0)$ . Although this indeed induces exponential relaxation of the volume-expansion order parameter profile, this relaxation occurs toward an equilibrium profile satisfying  $\gamma(\eta - \eta_0) = \Gamma_\eta \frac{\delta G}{\delta \eta}$ , rather than toward the initial profile  $\eta_0(z_0)$ . Although we can resolve this point by making the relaxational term an increasing function of the time t, such that the relaxational term dominates in the long-time limit, this introduces a different problem. Namely, if we apply an alternating electric field to the liquid crystal network, we expect this to eventually result in a steady-state expansion of the liquid crystal network, as reported in experiments [4, 9, 10]. However, a relaxational term that increases monotonically with t suppresses any volume expansion if we wait long enough, rendering a dynamic steady state impossible in the long term. Thus, we require a more sophisticated relaxation function,  $\tau(z_0, t)$  [s], which locally keeps track of the deformation history of the liquid crystal network to determine how strongly a given volume element should relax [1]. This is a highly non-trivial component of the theory, and although it is not a true memory kernel, it fulfils a similar function.

As the basis for this relaxation function we take  $\tau (z_0, t) = t$ , which describes Gaussian relaxation. This is the simplest functional form that invariably achieves relaxation of the volume-expansion order parameter to its initial profile in the long-time limit. To circumvent the suppression of volume expansion in this limit, we alter this function by following the philosophy that the relaxation of any element of expanded volume,  $\eta (z_0, t) > 0$ , is proportional to how long it has been in the expanded state. Numerically, we implement this through the recurrence relation

$$\tau(t, z_0) = t - \frac{1}{\eta(z_0, t)} \Big( \eta(z_0, t - \Delta t) [t - \tau(z_0, t - \Delta t)] \\ + |\eta(z_0, t) - \eta(z_0, t - \Delta t)| t \Big), \quad t \ge \Delta t, \quad (5)$$

where  $\Delta t$  denotes the numerical time increment. This means the relaxation function  $\tau (z_0, t)$  describes Gaussian relaxation at its core, but is increasingly attenuated the shorter the volume element in question has been in the expanded state. To account for this, the second term in Eq. (5) represents the time at which the volume element effectively entered the current expanded state. We achieve this by performing an average weighted by the magnitude of expansion at the previous time step (left-most term in brackets), and the magnitude of the changes in expansion that have occurred since (right-most term in brackets). This protocol naturally resets the relaxation function if the liquid crystal network relaxes back toward its initial configuration, and so permits steady-state oscillations. Although it is possible to achieve a similar effect using different protocols, we have chosen our approach under the aspect of simplicity. Our relaxation function  $\tau (z_0, t)$  is uniquely determined by temporal evolution of the volume-expansion order parameter profile  $\eta (z_0, t)$ , and represents a dynamical coupling that goes beyond the free-energetic nature of the Landau theory.

The above enables us to study the dynamical behaviour of the model. Finally, we reduce the parameter space of the model by introducing a dimensionless scaling.

#### III. SCALING PROCEDURE

We scale the theory by introducing the dimensionless volume-expansion order parameter  $\tilde{\eta} \equiv \eta/\eta (L_0)$ ; we do not scale the population order parameter f [-] so that we can explicitly maintain the constraint  $0 \leq f^2 \leq 1$ . Next, we identify  $H_*$  [J/m<sup>3</sup>] as the relevant energy scale of the problem, and define the scaled field strength  $h = (H - H_*)/H_*$ , as well as the scaled bulk modulus  $\tilde{B}_f = B_f/H_*$  and coupling constant  $\zeta = \xi^2/B_\eta H_*$ . Following this, we scale the spatial coordinate  $z_0$  to the reference thickness of the film,  $\tilde{z}_0 = z_0/L_0$ , from which the scaled square-gradient coefficients  $\tilde{\kappa}_f = \kappa_f/\sqrt{H_*L_0^2}$  and  $\tilde{\kappa}_{\tilde{\eta}} = \kappa_{\eta}/\sqrt{H_*B_{\eta}^2L_0^2/\xi^2}$  follow naturally.

For the scaling of the dynamical model parameters, we opt to set  $\tilde{\Gamma}_{\tilde{\eta}} = 1$ , and measure time relative to the evolution of the volume-expansion order parameter  $\tilde{\eta}$ . It then follows that the time scale of the problem becomes  $\tilde{t} = tB_{\eta}^{2}H_{*}\Gamma_{\eta}/\xi^{2}$ , and we write the scaled relaxation function  $\tilde{\tau} = \tau B_{\eta}^{2}H_{*}\Gamma_{\eta}/\xi^{2}$ . Upon inserting these scalings into the dynamical equations, Eq. (4), we read off the effective kinetic coefficient of the population order parameter,  $\tilde{\Gamma}_{f} = \Gamma_{f}\xi^{2}/\Gamma_{\eta}B_{\eta}^{2}$ , and the effective coefficient for viscoelastic relaxation,  $\tilde{\gamma} = \gamma\xi^{4}/B_{\eta}^{4}H_{*}^{2}\Gamma_{\eta}^{2}$ . For the purpose of this paper, we choose parameter values in the broad regime  $\tilde{\Gamma}_{f} < \tilde{\Gamma}_{\tilde{\eta}}$ , which in a previous publication [2] we have shown to be qualitatively in line with the experiments of Liu and co-workers [4], as well as our own molecular dynamics computer simulations [2].

This establishes the full theory used in the main text, where we drop the tildes for notational simplicity.

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this relationship becomes linear in the limit of strong electric fields, this does not alter our qualitative conclusions in this paper.

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