

Random networks of cross-linked directed polymersStephan Ulrich,¹ Annette Zippelius,^{1,2} and Panayotis Benetatos^{1,3}¹*Institute for Theoretical Physics, Georg-August-Universität-Göttingen, Friedrich-Hund-Platz 1, 37077 Göttingen, Germany*²*Max Planck Institute for Dynamics & Self-Organization, Bunsenstr. 10, 37073 Göttingen, Germany*³*Theory of Condensed Matter Group, Cavendish Laboratory, University of Cambridge, 19 J. J. Thomson Avenue, Cambridge CB3 0HE, United Kingdom*

(Received 17 November 2009; revised manuscript received 15 January 2010; published 19 February 2010)

We explore the effect of random permanent cross-links on a system of directed polymers confined between two planes with their end points free to slide on them. We treat the cross-links as quenched disorder and we use a semimicroscopic replica field theory to study the structure and elasticity of this system. Upon increasing the cross-link density, we get a continuous gelation transition signaled by the emergence of a finite in-plane localization length. The distribution of localization length turns out to depend on the height along the preferred direction of the directed polymers. The gelation transition also gives rise to a finite in-plane shear modulus which we calculate and turns out to be universal, i.e., independent of the energy and length scales of the polymers and the cross-links. Using a symmetry argument, we show that cross-links of negligible extent along the preferred axis of the directed polymers do not cause any renormalization to the tilt modulus of the uncross-linked system.

DOI: [10.1103/PhysRevE.81.021802](https://doi.org/10.1103/PhysRevE.81.021802)

PACS number(s): 61.41.+e, 61.43.-j, 62.20.D-, 82.70.Gg

I. INTRODUCTION

The statistical mechanics of directed polymers (DPs) has been a very active field of research for more than twenty years [1,2]. The directed paths under study may represent configurations of “real” extended one-dimensional objects such as polymers [3] and vortex lines in type-II superconductors [4], or may represent configurations in abstract spaces such as those used to model sequence alignment in bioinformatics [5].

Many physical systems consist of aligned extended one-dimensional building blocks which can have crystalline or fluidlike order in the transverse plane. Examples include columnar phases of DNA [6], discotic [7] or micellar [8] liquid crystals, ferrofluids [9], and electrorheological fluids [10]. In addition, polymer brushes consisting of dense flexible chains terminally anchored on a surface are characterized by chain elongation in the direction of the surface normal [11]. Although the chains of polymer brushes can assume backtracking conformations, under strong stretching they can be viewed as directed strings of Pincus blobs [12]. In recent years, there has been interest in cross-linked polymer brushes because of promising technological applications [13,14].

The effect of quenched disorder in the embedding medium on arrays of interacting directed elastic lines has led to the prediction of a whole zoo of glassy states in high- T_c superconductors [4]. In real polymer systems, irreversible cross-links can be viewed as quenched disorder of a different type and their effect can be studied using the tools of the statistical mechanics of disordered systems [15]. A replica field theory has been used to study the gelation transition due to permanent random cross-links in systems comprised of Gaussian chains [16], beads-and-springs [17], dimers-and-springs [18], p -beine [19], and wormlike chains [20]. A similar field-theoretic approach to well-cross-linked macromolecular networks has been developed by Panyukov and Rabin. [21,22]

In this paper, we employ the same theoretical framework to study the effect of permanent cross-links on a melt of flexible directed polymers in a particularly simple geometry. The polymers are stretched between two parallel flat surfaces with their ends free to slide on them. We predict a gelation transition upon cross-linking associated with the emergence of a finite localization length in the transverse plane which depends on the distance from the boundary surfaces of the slab.

Furthermore, we investigate mechanical properties of the system. Due to the asymmetry of the system, one has to distinguish between *tilt modulus* and *shear modulus*; the first one describes the resistance to shear of the boundaries in the preferred chain direction and the latter of the perpendicular boundaries. Remarkably, the tilt modulus remains completely unaffected upon cross-linking with cross-links of negligible extent in the aligning direction.

The paper is organized as follows. We present our model in Sec. II. In Sec. III, we define and calculate the tilt modulus for the cross-linking geometry of our model. We construct a replica field theory and obtain the gelation transition in Sec. IV. The shear modulus is discussed in Sec. V. We summarize in Sec. VI.

II. MODEL

We consider N directed polymers stretched between two planes spaced a distance L apart. The end points of the polymers are free to slide on the planes. Each polymer configuration is described by a curve (path) $\mathbf{r}(z)=(x(z), y(z))$, where $z \in [0, L]$ and z is the direction of alignment (Fig. 1). By the definition of directedness, these paths exclude loops and overhangs. The areal density of the system in the xy plane is N/A . We assume free boundary conditions at $z=0$ and $z=L$, allowing the polymer ends to assume any arbitrary position on the corresponding planes with any slope. In the absence

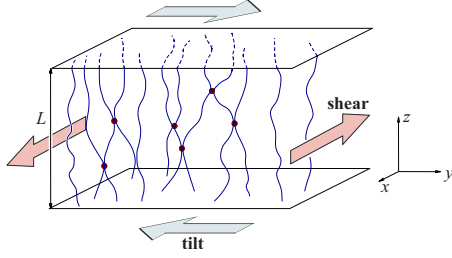


FIG. 1. (Color online) A schematic diagram of directed polymers in a slab of thickness L . z is the preferred direction and we refer to x, y as the *transverse* or *in-plane* direction.

of cross-links, the effective free-energy functional (“Hamiltonian”) of the directed polymers consists of two terms,

$$\mathcal{H}_0\{\mathbf{r}_i(z)\} = \sum_{i=1}^N \frac{\sigma}{2} \int_0^L dz \left(\frac{d\mathbf{r}_i(z)}{dz} \right)^2 + \sum_{i<j} \frac{\lambda}{2} \int_0^L dz \delta(\mathbf{r}_i(z) - \mathbf{r}_j(z)), \quad (1)$$

where the first term penalizes tilting away from the z direction with σ being the effective line tension and the second term is an excluded volume interaction.

A physical system where the effective free energy of Eq. (1) can be realized is that of strongly stretched wormlike chains of contour length L . If the two plates are held apart by a pressure P and the areal density (on the xy plane) of the polymers is high, each polymer will be stretched by a tension $\mathcal{F} \approx PA/N$. A strong tension allows only weakly tilting configurations. In this case, the aligning part of the free energy reads

$$\mathcal{H}_{al}^{(1)}\{\mathbf{r}_i(z)\} = \sum_{i=1}^N \frac{\mathcal{F}}{2} \int_0^L dz \left(\frac{d\mathbf{r}_i(z)}{dz} \right)^2 + \sum_{i=1}^N \frac{\kappa}{2} \int_0^L dz \left(\frac{d^2\mathbf{r}_i(z)}{dz^2} \right)^2, \quad (2)$$

where κ is the bending stiffness of the wormlike chains related to their persistence length L_p via $\kappa = L_p k_B T$. For $\mathcal{F} \gg (k_B T)^2 / \kappa$ and $L \gg L_p$, one can show [23] that the bending term on the rhs of the previous equation can be neglected and the projection of the polymer on the xy plane behaves as a Gaussian chain.

In Ref. [12], a realization of a stretched brush is envisioned as *ABA* triblock lamellae with selective cross-linking of the *A* blocks. In an analogous realization of our model, the *A* blocks would form fluid membranes.

Another physical realization of Eq. (1) is that of wormlike chains interacting with a strong nematic field [2,3]. If the chains are embedded in a nematic solvent with very large Frank constants and the effective tension due to the polymer-nematic interaction σ is such that $\sigma \gg (k_B T)^2 / \kappa$, hairpins are negligible. If, in addition, $L \gg L_p$, the bending stiffness can be neglected altogether and the chains behave as directed flexible polymers.

In the system described by Eq. (1), we introduce M permanent cross-links which restrict linked polymer segments to remain within a distance of order a . Their effect is described by an effective interaction,

$$\frac{\mathcal{H}(C_M)}{k_B T} = \frac{1}{2a^2} \sum_{e=1}^M (\mathbf{r}_{i_e}(z_e) - \mathbf{r}_{j_e}(z_e))^2. \quad (3)$$

$C_M := \{i_e, j_e; z_e\}$ is a quenched configuration of M cross-links identified by the polymers i_e, j_e involved and the cross-linking height z_e . For the sake of simplicity, we assume that the cross-linking interaction is “local” in the z direction and only depends on the in-plane distance of the polymer segments. As we shall show in Sec. III, this assumption has profound consequences for the elasticity of the cross-linked system.

The partition function of the system for a specific realization of cross-links, C_M , reads as

$$Z(C_M) = \left\langle \exp\left(-\frac{\mathcal{H}(C_M)}{k_B T}\right) \right\rangle, \quad (4)$$

where $\langle \dots \rangle$ denotes average over all polymer configurations with Boltzmann weight $\exp(-\mathcal{H}_0/k_B T)$. Physical observables of interest can be calculated from the quenched-disorder averaged free energy, $F = -k_B T [\ln Z]$, where $[\dots]$ denotes average over all realizations of random cross-links. We assume that the number of cross-links can vary and a realization with M cross-links follows the Deam-Edwards distribution [15],

$$P(C_M) \propto \frac{1}{M!} \left(\frac{\mu^2 A}{2N(2\pi a^2)} \right)^M Z(C_M). \quad (5)$$

The parameter $\mu^2 = 2[M]/N$ controls the average number of cross-links per polymer, and the physical meaning of this distribution is that polymer segments close to each other in the uncross-linked phase have a high probability of getting linked.

III. TILT MODULUS

On large length scales, an array of directed polymers can be described as an elastic continuum with three elastic moduli: a shear, a bulk, and a tilt modulus. The first two characterize deformations in the transverse plane whereas the third characterizes the response to tilting away from the preferred axis. The elastic free energy of such a system was proposed in the context of vortex-line arrays in type-II superconductors by de Gennes and Matricon [24]:

$$F_{el} = \frac{1}{2} \int \frac{d^2q}{(2\pi)^2} \int \frac{dq_z}{2\pi} \{ (Kq_z^2 + Gq^2) |\mathbf{u}(\mathbf{q}, q_z)|^2 + Bq_\mu q_\nu \mu_\mu(\mathbf{q}, q_z) u_\nu(-\mathbf{q}, -q_z) \}, \quad (6)$$

where K , G , and B are, respectively, the tilt, shear, and bulk modulus. μ, ν are Cartesian indices in the xy plane. $\mathbf{u}(\mathbf{q}, q_z)$ is the Fourier transform of the two-component displacement field which parametrizes the elastic distortion of the vortex-line array.

In order to measure the tilt modulus, we consider a small force, \mathbf{f} , applied at the upper end point of each polymer and

the opposite force, $-\mathbf{f}$, applied at the lower end point. The induced deformation is measured by the average tilt field. The tilt field is defined as

$$\mathbf{t}(\mathbf{r}, z) = \sum_{i=1}^N \frac{d\mathbf{r}_i}{dz} \delta(\mathbf{r} - \mathbf{r}_i(z)). \quad (7)$$

The energy of the system subject to a cross-link configuration C_M and to a tilting force \mathbf{f} reads as

$$\mathcal{H}_{\mathbf{f}} = \mathcal{H}_0 + \mathcal{H}(C_M) - \int_0^L dz \int d^2r \mathbf{f} \cdot \mathbf{t}(\mathbf{r}, z). \quad (8)$$

To leading order in \mathbf{f} , the average tilt field is

$$\frac{1}{LA} \int_0^L dz \int d^2r \langle \mathbf{t}(\mathbf{r}, z) \rangle_{\mathbf{f}} = \frac{1}{K} \mathbf{f}, \quad (9)$$

where $\langle \dots \rangle_{\mathbf{f}}$ denotes thermal average with a Boltzmann weight corresponding to the energy functional $\mathcal{H}_{\mathbf{f}}$. The tilt modulus, K , can be extracted from the partition function as a static linear-response coefficient,

$$\frac{1}{K} \delta_{\mu\nu} = \frac{k_B T A}{N^2 L} \left. \frac{\delta^2}{\delta f_\mu \delta f_\nu} \ln Z_{\mathbf{f}} \right|_{\mathbf{f}=0}, \quad (10)$$

where

$$Z_{\mathbf{f}} = \int \mathcal{D}\{\mathbf{r}_i(z)\} \exp\left(-\frac{\mathcal{H}_{\mathbf{f}}\{\mathbf{r}_i(z)\}}{k_B T}\right). \quad (11)$$

In the path integral of the previous equation, we apply a ‘‘Galilean’’ transformation (where the height z is viewed as a timelike parameter) [25],

$$\begin{aligned} \mathbf{r}_i &\rightarrow \mathbf{r}'_i = \mathbf{r}_i + \frac{\mathbf{f}}{\sigma} z \\ z &\rightarrow z' = z \end{aligned} \quad (12)$$

which brings it to the form

$$Z_{\mathbf{f}} = Z_{\mathbf{f}=0} \exp\left(-\frac{NL}{2k_B T \sigma} \mathbf{f}^2\right), \quad (13)$$

where $Z_{\mathbf{f}=0}$ is the partition function without the external field \mathbf{f} . Equations (13) and (10) yield

$$K = \frac{N}{A} \sigma. \quad (14)$$

This result implies that the tilt modulus of a directed polymer array with a specific realization of cross-links of the type described by Eq. (3) is completely unaffected by the cross-links and simply reduces to the single-polymer tension. Since any realization of the quenched disorder associated with the cross-links of this type would give the same result, we are spared the burden of having to use replicas for the calculation of the average over disorder.

The reason behind the particularly simple result for the tilt modulus is the ‘‘Galilean’’ invariance of the interactions between the polymers as well as of the boundary conditions. In the specific model, both the excluded volume interaction and

the cross-link interaction involve polymer segments at the same height z and therefore remain unchanged under a ‘‘Galilean’’ transformation. Real cross-linking molecules have a finite extent and may link to polymer segments at different heights thus breaking the ‘‘Galilean’’ invariance. That would lead to a nontrivial renormalization of the tilt modulus. In the limiting case of cross-links with negligible extent, our model is a good approximation, and we expect the tilt modulus to remain unchanged and be given by Eq. (14).

IV. GELATION TRANSITION

The system of cross-linked directed polymers undergoes a gelation transition as the number of cross-links per chain increases. Whereas in the sol phase the DPs are free to move in the xy plane like particles in a two-dimensional fluid, the polymers’ motion in the gel phase is restricted to finite excursions around preferred positions. Thus there is a localization transition in the xy plane, similar to the gelation transition in systems comprised of other building blocks in $d=3$ [16]. Since the latter has been discussed extensively, we keep our discussion short.

What is the *order parameter* for the localization transition in the xy plane? A point z on curve i , i.e., monomer z on polymer i in a discretized model, is localized, if it has a nontrivial expectation value

$$\langle \delta(\mathbf{x} - \mathbf{r}_i(z)) \rangle \neq 1/V. \quad (15)$$

If the particles are localized at random positions, as we expect for the gel phase, then the density averaged over all particles vanishes at any nonzero wave vector. A possible order parameter is the second moment of the local density:

$$\Omega^{(2)}(\mathbf{q}, z) = \frac{1}{N} \sum_{i=1}^N [\langle e^{i\mathbf{q} \cdot \mathbf{r}_i(z)} \rangle \langle e^{-i\mathbf{q} \cdot \mathbf{r}_i(z)} \rangle]. \quad (16)$$

In general, one polymer is cross-linked with a finite number of other polymers and in fact close to the transition this number is small. Hence there is no reason to expect that the local density should obey Gaussian statistics, therefore we need all moments of the local density to characterize the gel. This is achieved in the replica formalism by introducing n copies, one for each thermal expectation value. The order parameter in the replica theory

$$\Omega(\mathbf{x}_1 \dots \mathbf{x}_n, z) = \frac{1}{N} \sum_{i=1}^N [\langle \delta(\mathbf{x}_1 - \mathbf{r}_i(z)) \rangle \dots \langle \delta(\mathbf{x}_n - \mathbf{r}_i(z)) \rangle],$$

captures all moments of the local density and hence characterizes the structure completely.

The average over the quenched realizations of cross-links, C_M , is done with help of the replica trick. The disorder averaged free energy $F = -k_B T [\ln Z] = \lim_{n \rightarrow 0} (\mathcal{Z}_{n+1} - \mathcal{Z}_1) / (n \mathcal{Z}_1)$ is represented in terms of n noninteracting copies of the system together with one additional replica to account for the distribution $P(C_M)$ of Eq. (5) which is proportional to the partition function. The replicated partition function is represented as a functional integral over collective fields $\Omega(\hat{q}, z)$,

$$\mathcal{Z}_{n+1} = \int \mathcal{D}\Omega e^{-N f_{n+1}}, \quad (17a)$$

$$\begin{aligned}
 f_{n+1}(\Omega) &= \phi^n \frac{\mu^2}{2L} \int_0^L dz \sum_{\hat{q} \in \text{HRS}} |\Omega(\hat{q}, z)|^2 \Delta(\hat{q}) \\
 &+ \frac{1}{2L} \int_0^L dz \sum_{\hat{q} \in \text{IRS}} |\Omega(\hat{q}, z)|^2 \tilde{\lambda}(\hat{q}) - \ln \mathfrak{z},
 \end{aligned} \tag{17b}$$

with the single-polymer partition function

$$\begin{aligned}
 \mathfrak{z} &= \int \mathcal{D}\hat{r}(z) e^{-H_0^{(n+1)}} \exp\left(\frac{\phi^n \mu^2}{L} \int_0^L dz \sum_{\hat{q} \in \text{HRS}} \Delta(\hat{q}) \Omega(\hat{q}, z) e^{-i\hat{q}\cdot\hat{r}(z)}\right. \\
 &\left. + \frac{i}{L} \int_0^L dz \sum_{\hat{q} \in \text{IRS}} \tilde{\lambda}(\hat{q}) \Omega(\hat{q}, z) e^{-i\hat{q}\cdot\hat{r}(z)}\right),
 \end{aligned} \tag{18}$$

where

$$\tilde{\lambda}(\hat{q}) := \lambda \frac{LN}{2A} - \phi^n \mu^2 \Delta(\hat{q}). \tag{19}$$

To simplify the notation we have introduced hatted vectors, such as $\hat{q} := (\mathbf{q}_0, \mathbf{q}_1, \dots, \mathbf{q}_n)$ for $(n+1)$ -fold replicated vectors. We have also adopted units of energy such that $k_B T \equiv 1$. The harmonic potential for the cross-links is reflected in $\Delta(\hat{q}) = \exp(-a^2 \hat{q}^2 / 2)$ and $\phi = 2\pi a^2 / A$. The collective field Ω is almost the order parameter, discussed above, except for the zeroth replica which we have introduced to account for the disorder average [...] in Eq. (17).

Areal density fluctuations are represented by $\Omega(\hat{q}, z)$ with $\hat{q} = (\mathbf{0}, \dots, \mathbf{q}_\alpha, \dots, \mathbf{0})$, i.e., only one nonzero component (IRS). These fluctuations are penalized by the excluded volume interaction. The stability of the liquid state in mean-field approximation (uniform density) is controlled by the coefficient of the quadratic term in the fluctuations. A sufficiently strong excluded volume interaction such that $\tilde{\lambda}(\hat{q}) \gg 1$ together with the positive definiteness of the kernel (in z_1, z_2) $\langle e^{-i\hat{q}\cdot(\hat{r}(z_1) - \hat{r}(z_2))} \rangle = \exp(-\hat{q}^2 |z_1 - z_2| / 2\sigma)$ preclude a collapse of the liquid state. Since the areal density fluctuations are non-critical, we only consider the order parameter in the so-called higher replica sector (HRS) consisting of vectors \hat{q} with at least two nonzero components.

The expectation value of the order-parameter field

$$\langle \Omega(\hat{x}, z) \rangle_f = \langle \delta(\hat{x} - \hat{r}(z)) \rangle_f \tag{20}$$

has to be calculated self-consistently with the weight of Eq. (17). Here we restrict ourselves to the saddle-point approximation $\delta f_{n+1} / \delta \Omega = 0$. As for the gel transition of random coils, the saddle-point equation is solved exactly by the following ansatz for the order parameter:

$$\Omega(\hat{q}, z) = (1 - Q) \delta_{\hat{q}, \hat{0}} + Q \delta_{\mathbf{q}_\alpha, \mathbf{0}} \int_0^\infty d\xi^2 \mathcal{P}(\xi^2, z) \exp\left(-\frac{\hat{q}^2 \xi^2}{2}\right). \tag{21}$$

Here Q denotes the fraction of DPs in the infinite cluster and hence $1 - Q$ is the fraction of DPs in the fluid state, giving rise to the first (trivial) contribution to the order parameter. On the other hand, the localized particles are characterized by the localization length ξ , which fluctuates not only from

polymer to polymer but also along one directed polymer giving rise to a distribution of localization length

$$\mathcal{P}(\xi^2, z) = \frac{1}{QN} \sum_{j \in Q} \langle \delta(\xi^2 - \xi_j^2(z)) \rangle \tag{22}$$

which depends on z . After averaging over the disorder the system still has macroscopic translational invariance in the xy plane. This requires that $\mathbf{q}_\parallel := \sum_{\alpha=0}^n \mathbf{q}_\alpha = \mathbf{0}$.

The solution of the saddle-point equation reveals a gel transition at a critical cross-link concentration $\mu^2 = 1$, when a macroscopic cluster of cross-linked DPs is formed. The gel transition is signaled by a nonzero value of the gel fraction Q . Close to the gel transition, $\epsilon = \mu^2 - 1 \ll 1$ grows continuously from zero: $Q = 2\epsilon + \mathcal{O}(\epsilon^2)$. To discuss the distribution of localization length, we note that we have several length scales in our system: the internal length of a directed polymer, L , the length of a cross-link, a , and the radius of gyration in the xy plane, which is determined by $l := \sqrt{L/(2\sigma)}$. We expect that the latter will set the scale for the localization length, introduce the abbreviation $\theta = (2/3 + a^2/l^2)l^2/(\xi^2\epsilon)$ and consider the distribution of rescaled, inverse localization length, $\pi(\theta, s) = \pi(z/L)$, with

$$\pi(\theta, s) d\theta = \mathcal{P}(\xi^2, Ls) d\xi^2. \tag{23}$$

This function is the solution of

$$\begin{aligned}
 (1 + 2\epsilon)\pi(\theta, s) &= (1 + \epsilon) \int_0^1 ds_1 \pi(\theta, s_1) \\
 &+ \frac{\epsilon}{2/3 + a^2/l^2} \int_0^1 ds_1 \partial_\theta (\theta^2 \pi(\theta, s_1)) \{2|s - s_1| + a^2/l^2\} \\
 &+ \epsilon \int_0^1 ds_1 ds_2 \int_0^\theta d\theta_1 \pi(\theta_1, s_1) \pi(\theta - \theta_1, s_2) + \mathcal{O}(\epsilon^2).
 \end{aligned} \tag{24}$$

To gain a better understanding of the solution, we decompose the distribution into its mean with respect to s , $\bar{\pi}(\theta) = \int ds \pi(\theta, s)$ and a deviation: $\pi(\theta, s) = \bar{\pi}(\theta) + \delta\pi(\theta, s)$. The mean, $\bar{\pi}(\theta)$, fulfills the same equation as for isotropic gels [16]. The deviation is small close to the gel point,

$$\delta\pi(\theta, s) = \epsilon w(s) \partial_\theta (\theta^2 \bar{\pi}(\theta)) + \mathcal{O}(\epsilon^2), \tag{25}$$

$$w(s) = \frac{s^2 + (1 - s)^2 - 2/3}{a^2/l^2 + 2/3}, \tag{26}$$

and furthermore controlled by the ratio of cross-link length to in-plane radius of gyration: $a_l^2 := a^2/l^2$. The larger the radius of gyration l , the more pronounced is the dependence on s . We show the distribution for a typical value $a_l^2 = 0.1$ in Fig. 2. As one would expect, localization is strongest in the middle of the directed polymer and weaker at the boundaries. The variation across the length of the DPs is stronger for larger localization length (small θ).

To get a better understanding of this anisotropy, we show in Fig. 3 cuts of Fig. 2 for two fixed θ values. As one can see,

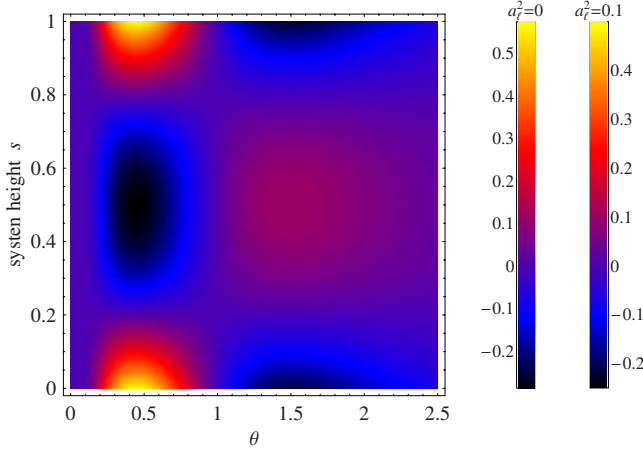


FIG. 2. (Color online) Height-dependent part, $\delta\pi(\theta, s)$, of the distribution of inverse localization length, θ , as a function of θ and $s:=z/L$. Due to the scaling behavior close to the sol-gel transition, $\delta\pi(\theta, s)$ is normalized with ϵ . a_7^2 is the ratio squared of the in-plane extent of a cross-link to the in-plane radius of gyration of a free DP.

large localization lengths (such as $\theta=1/2$, solid red curve) are favored at the boundaries ($s \approx 0, 1$), and small localization lengths (such as $\theta=2$, dashed blue curve) in the middle of the sample ($s \approx 1/2$). This behavior is reasonable since the ends of the chains are more loose. A chain segment close to the top (bottom) boundary has a lower probability to have a cross-link above (below) and hence is on average less localized than a chain segment in the middle.

V. SHEAR MODULUS

In the gel phase, the DPs are localized in the xy plane. Hence the symmetry with respect to translations in the x and y directions is spontaneously broken as indicated by a non-trivial expectation value of the local density as defined in Eq. (15). The symmetry breaking occurs on a local level only, while the macroscopic system (averaged over the cross-link related disorder) remains homogeneous. We expect low-energy Goldstone fluctuations and a finite stiffness to static shear deformations in the xy plane (see Fig. 1). In the replica formalism, the overall macroscopic translational invariance is reflected in common translations of all $n+1$ replicas,

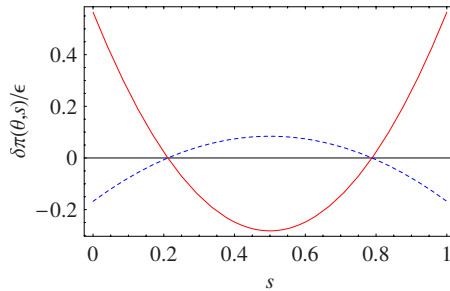


FIG. 3. (Color online) Height-dependent part, $\delta\pi(\theta, s)$, of the distribution of inverse localization length, θ vs the normalized system height $s=z/L$, for $\theta=1/2$ (solid, red) and $\theta=2$ (dashed, blue). The cross-link extent is $a^2=0$ for both graphs. As in Fig. 2, $\delta\pi(\theta, s)$ is scaled with ϵ .

whereas replica-dependent translations generate a family of order parameters which all give rise to the same free energy.

To investigate the response of the system to shear deformations, we start from the replica free energy [Eq. (17b)] and consider fluctuations around saddle point (21), which correspond to long-wavelength shear deformations $\mathbf{u}^\alpha(\mathbf{r})$ in each replica $\alpha=1, \dots, n$ except the zeroth replica [17,26,27]. The latter represents the preparation state before the cross-linking process, which takes place in a state without shear deformations. We furthermore want to consider pure shear only and hence require that volume is conserved, $\nabla \cdot \mathbf{u}^\alpha = 0$, and no tilt deformations are excited; i.e., $\mathbf{u}^\alpha(\mathbf{r})$ are chosen to be independent of z .

The order parameter for the deformed state thus reads as

$$\begin{aligned} \Omega_\mu(\hat{q}, z) = & (1 - Q) \delta_{\hat{q}, \hat{0}} \\ & + Q \int \frac{d^2 r}{A} \exp\left(i \mathbf{q}_\parallel \cdot \mathbf{r} + i \sum_{\alpha=1}^n \mathbf{q}_\perp^\alpha \cdot \mathbf{u}^\alpha(\mathbf{r})\right) \\ & \times \int_0^\infty d\xi^2 \mathcal{P}(\xi^2, z) \exp\left(-\frac{\hat{q}^2 \xi^2}{2}\right), \end{aligned} \quad (27)$$

where $\mathbf{q}_\perp^{(\alpha)} := \mathbf{q}^{(\alpha)} - \frac{1}{n+1} \mathbf{q}_\parallel$. If the deformations are taken to be spatially uniform we recover the general solution of the saddle-point equation. Fluctuations around the saddle-point value are incorporated by nonzero $\partial_x \mathbf{u}$ and $\partial_y \mathbf{u}$. These are assumed to be small, corresponding to long-wavelength excitations.

We plug the ansatz (27) into the free energy (17b) and only keep the lowest order in Q and in the derivatives $\partial_x \mathbf{u}$ and $\partial_y \mathbf{u}$. Higher order derivatives, such as $\partial_{x,y}^2 \mathbf{u}$, are neglected. The result has the form of an elastic free energy of an incompressible medium,

$$f_{n+1}(\Omega_\mu) = f_{\text{sp}} + \frac{G}{2N} \int d^2 r \sum_{\mu, \nu=1}^2 \sum_{\alpha=1}^n \left(\frac{\partial u_\nu^\alpha}{\partial r_\mu} \right)^2. \quad (28)$$

There f_{sp} is the saddle-point value of the free energy and G is the shear modulus,

$$G = \left(\frac{Q^2(\mu^2 - 1)}{2} - \frac{Q^3}{6} \right) \frac{N}{A} k_B T. \quad (29)$$

With the distance from the sol-gel transition $\epsilon = \mu^2 - 1$, the relation $Q = 2\epsilon + \mathcal{O}(\epsilon^2)$ found in the previous section, and the areal density $n_0 := N/A$ of the polymer chains, the shear modulus simplifies to

$$G = \frac{2}{3} \epsilon^3 n_0 k_B T. \quad (30)$$

The scaling of the shear modulus $G \propto \epsilon^3$ close to the sol-gel transition is in agreement with previous results for isotropic systems [17,26,27]. This result for the shear modulus is universal and does not depend on the microscopic length or energy scales which characterize the polymers and the cross-links.

VI. CONCLUSIONS AND OUTLOOK

We have addressed the effect of random permanent cross-links on an array of directed polymers confined between two planes with their end points free to slide on them. The cross-links are assumed to have negligible extent in the preferred direction of the DPs (local in the z direction), but they are springlike in the transverse (xy) plane. The constraints imposed by the cross-links are treated as quenched disorder which follows the Deam-Edwards distribution.

At a certain critical cross-link density, there is a continuous gelation transition from a sol phase where the DPs are free to wander in the x and y directions to a gel characterized by the emergence of finite localization lengths for the polymer segments which belong to the infinite percolating cluster. Unlike other isotropic polymer systems which undergo a similar transition, the DPs are inherently anisotropic and this is reflected in the height (z) dependence of the order parameter and the associated distribution of localization length. Because of the finite extent of the system in the preferred direction, larger localization lengths are favored closer to the boundaries where the polymer end points are free to slide.

The gelation transition is accompanied by the emergence of a finite shear modulus. Our result for the array of cross-linked DPs close to the gel point agrees with previous results for isotropic systems thus suggesting universality. As far as in-plane localization and the relevant shear modulus are concerned, our system can be viewed as effectively two dimensional. It is well known that truly long-ranged positional order cannot exist in two dimensions [2]. In [27], it was shown

for isotropic systems that fluctuations drive the order parameter to zero as expected from the Mermin-Wagner theorem. Yet a quasicrystalline solid state survives. It is characterized by a finite stiffness to static shear deformations and algebraically decaying correlations.

The asymmetry of our system due to the preferred direction of the DPs entails the existence of a tilt modulus which is different and independent from the shear modulus. We have only considered the simplest case of cross-links with negligible extent in the preferred direction of the DPs. Using a “Galilean” invariance argument, we have shown that cross-links of this type leave the tilt modulus of the uncross-linked system completely unaffected. We expect cross-links which connect polymer segments at different heights to induce an effective “nonlocal in z ” interaction between the connected polymers. By analogy to a similar interaction in the case of flux lines in type-II superconductors [28], we can expect the breaking of the “Galilean” invariance to cause an upward renormalization (stiffening) of the tilt modulus. This putative renormalization may be useful to quantify the cross-link induced collapse of polymer brushes. We hope to report on these issues in a future publication.

ACKNOWLEDGMENTS

We gratefully acknowledge financial support by the DFG through Grant No. SFB 602. P.B. acknowledges support during the later part of this work by EPSRC-GB via the University of Cambridge TCM Programme Grant.

-
- [1] M. Kardar, *Statistical Physics of Fields* (Cambridge University Press, Cambridge, 2007).
- [2] D. R. Nelson, *Defects and Geometry in Condensed Matter Physics* (Cambridge University Press, Cambridge, 2002).
- [3] R. D. Kamien, P. Le Doussal, and D. R. Nelson, *Phys. Rev. A* **45**, 8727 (1992).
- [4] G. Blatter *et al.*, *Rev. Mod. Phys.* **66**, 1125 (1994).
- [5] T. Hwa, *Nature (London)* **399**, 17 (1999).
- [6] R. Podgornik, D. C. Rau, and V. A. Parsegian, *Macromolecules* **22**, 1780 (1989).
- [7] S. Chandrasekhar, B. K. Sadashiva, and K. A. Suresh, *Pramana* **9**, 471 (1977).
- [8] S. A. Safran, L. A. Turkevich, and P. Pincus, *J. Phys. (Paris), Lett.* **45**, 69 (1984).
- [9] R. E. Rosensweig, *Ferrohydrodynamics* (Cambridge University Press, Cambridge, 1985).
- [10] T. C. Halsey and W. Toor, *Phys. Rev. Lett.* **65**, 2820 (1990).
- [11] P. G. de Gennes, *Macromolecules* **13**, 1069 (1980).
- [12] A. Halperin and E. B. Zhulina, *Macromolecules* **24**, 5393 (1991).
- [13] D. M. Loveless *et al.*, *Angew. Chem., Int. Ed.* **45**, 7812 (2006).
- [14] P. Xu *et al.*, *Biomacromolecules* **5**, 1736 (2004).
- [15] R. T. Deam and S. F. Edwards, *Philos. Trans. R. Soc. London, Ser. A* **280**, 317 (1976).
- [16] P. M. Goldbart, H. Castillo, and A. Zippelius, *Adv. Phys.* **45**, 393 (1996).
- [17] S. Ulrich, X. Mao, P. M. Goldbart, and A. Zippelius, *Europhys. Lett.* **76**, 677 (2006).
- [18] X. Xing, S. Pfahl, S. Mukhopadhyay, P. M. Goldbart, and A. Zippelius, *Phys. Rev. E* **77**, 051802 (2008).
- [19] P. M. Goldbart and A. Zippelius, *Europhys. Lett.* **27**, 599 (1994).
- [20] P. Benetatos and A. Zippelius, *Phys. Rev. Lett.* **99**, 198301 (2007).
- [21] S. V. Panyukov and Y. Rabin, *Phys. Rep.* **269**, 1 (1996).
- [22] S. V. Panyukov and Y. Rabin, in *Theoretical and Mathematical Methods in Polymer Research*, edited by A. Y. Grosberg (Academic, New York, 1998).
- [23] P. G. de Gennes, in *Polymer Liquid Crystals*, edited by A. Ciferri, W. R. Kringbaum, and R. B. Meyer (Academic, New York, 1982), p. 115.
- [24] P. G. de Gennes and J. Matricon, *Rev. Mod. Phys.* **36**, 45 (1964).
- [25] U. C. Täuber and D. R. Nelson, *Phys. Rep.* **289**, 157 (1997).
- [26] S. Mukhopadhyay, P. M. Goldbart, and A. Zippelius, *Europhys. Lett.* **67**, 49 (2004).
- [27] P. M. Goldbart, S. Mukhopadhyay, and A. Zippelius, *Phys. Rev. B* **70**, 184201 (2004).
- [28] P. Benetatos and M. C. Marchetti, *Phys. Rev. B* **59**, 6499 (1999).