Self-Consistent Field Approach for Cross-Linked Copolymer Materials

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A generalized self-consistent field approach for polymer networks with a fixed topology is developed. It is shown that the theory reproduces the localization of cross-links, which is characteristic for gels. The theory is then used to study the order-disorder transition in regular networks of end-linked diblock copolymers. Compared to diblock copolymer melts, the transition is shifted towards lower values of the incompatibility parameter χ (the Flory- Huggins parameter). Moreover, the transition becomes strongly first order already at the mean-field level. If stress is applied, the transition is further shifted and finally vanishes in a critical point.

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Polymers are macromolecules made of a large number of structurally identical or similar subunits (monomers), with local monomer interactions that tend to be weak on the scale of the thermal energy $k_B T$. In polymeric materials, molecules typically have many interaction partners. Therefore, these systems can often be described quite satisfactorily by mean-field theories. In particular, the self-consistent field (SCF) theory [1–6] is a powerful mean-field approach for describing inhomogeneous polymer melts and solutions. Originally developed as a theory for interfaces between immiscible homopolymer phases [1], it has now become a standard tool for studying phase transitions between block copolymer mesophases [7–9], the self-organization of amphiphilic polymers in solution [10], or the structure of polymer composite materials [11–13], to name just a few examples. Numerous extensions have been proposed that allow one to include, e.g., orientational order [14], electrostatic interactions [15], dynamical processes [16–19], or the effect of fluctuations [20–22].

Despite these successes, the SCF theory still suffers from severe restrictions. Most prominently, it is limited to fluids. Polymers are taken to have full translational freedom and, consequently, the systems cannot sustain large shear stress or elastic deformations. Complex fluids may respond elastically to small stress to some extent, and this can be studied by SCF methods [23,24], but they necessarily yield to large stress. In reality, however, many materials of interest such as rubber are irreversibly cross-linked, either chemically or physically. Cross-linking is a popular strategy for stabilizing composite materials or polymeric nanostructures. While SCF approaches have been devised for describing systems of reversibly cross-linked polymeric materials [25–27], there exists so far no SCF theory for irreversibly cross-linked polymer networks.

In this Letter, we propose a way to overcome this limitation. We develop a SCF approach for irreversibly cross-linked networks with fixed (quenched) topology.

As an application example, we then use the method to study the phase behavior of symmetric cross-linked diblock copolymers. Specifically, we address the question of how cross-linking affects the order-disorder transition (ODT), i.e., the transition between a disordered state and an ordered microphase separated state. The microphase separation in fluids of diblock copolymers has been studied intensely by SCF methods [7–9]. According to mean-field theory, melts of symmetric diblock copolymers undergo a continuous microphase separation transition to an ordered lamellar phase upon cooling. Fluctuations shift the transition and it becomes weakly first order [22,28,29]. Whereas this is all well understood in polymer fluids, the situation in cross-linked systems is less clear.

Most theoretical studies of microphase separation in cross-linked polymer blends have focussed on situations where a blend of incompatible A and B polymers is first randomly cross-linked in a high-temperature homogeneous state and then cooled down. In a seminal paper, de Gennes predicted a spinodal instability with respect to microphase separation in such systems [30]. Several authors have built on this idea and investigated the instability by experiment [31], theory [32–36], and simulation [37,38]. The influence of random network forces on the structure of the ordered state was investigated by elasticity theories [39,40].

Here, we will consider a slightly different situation: We will study a diblock copolymer network cross-linked in a lamellar state, asking whether and how cross-linking stabilizes the lamellar structure. In computer simulations, Lay *et al.* [41] found that the lamellar order of loosely cross-linked ordered diblock copolymer melts disappears upon heating. We will investigate this phenomenon. More specifically, we will consider a regular network of end-linked diblock copolymers. Experimentally, the synthesis of such ideal copolymer networks is coming within reach [42], and simple phenomenological theories have been devised to predict the expected microphase separation [43,44]. A more refined SCF theory which can predict the phase behavior of such systems based on molecular parameters is thus clearly desirable.

To introduce the general formalism of the new SCF approach, we consider for simplicity a regular network without dangling ends, with connecting polymer strands made of different types of monomers $\alpha = A, B, \ldots$. The overall strand density is C. The system is defined by (i) the topology of the network, i.e., the set of cross-links l and linker connections $\langle jk \rangle$, (ii) the cross-link positions $\mathbf{r}_j$ and the conformations of linker strands, which we parametrize by space curves $\mathbf{R}_{jk}(s)$ with $s \in [0{:}1]$, and (iii) the sequence of monomers along the strands, described by characteristic functions $\eta_{jk}^{(\alpha)}(s)$, with $\eta_{jk}^{(\alpha)}(s) = 1$ if the chain is occupied by monomers of type α at the position s and $\eta_{jk}^{(\alpha)}(s) = 0$ otherwise $[\sum_\alpha \eta_{jk}^{(\alpha)}(s) \equiv 1]$. Strands are taken to be Gaussian chains with polymerization index N and statistical segment length b. The interaction between monomers is defined by an interaction potential $U[\{\hat{\Phi}_\alpha\}]$ which depends on the local monomer fractions $\hat{\Phi}_\alpha = (1/C)\sum_{\langle jk \rangle} \int_0^1 ds\, \delta(\mathbf{r} - \mathbf{R}_{jk}(s))\eta_{jk}^{(\alpha)}(s)$. In the following, we will mainly consider binary AB melts with Flory-Huggins interaction $U = C\int d\mathbf{r}\{\chi N \hat{\Phi}_A \hat{\Phi}_B + (\kappa N/2)(\hat{\Phi}_A + \hat{\Phi}_B - 1)^2\}$, where χ is the Flory-Huggins parameter and κ is related to the inverse compressibility of the melt. Here and in the following, the energy units are chosen such that $k_B T = 1$. The partition function of the whole system thus reads

$$\mathcal{Z} = \prod_l \int d\mathbf{r}_l \prod_{\langle jk \rangle} \int \mathcal{D}\mathbf{R}_{jk}\, \delta(\mathbf{r}_j - \mathbf{R}_{jk}(0))\delta(\mathbf{r}_k - \mathbf{R}_{jk}(1)) \times \exp\left\{ -\sum_{\langle mn \rangle} \frac{1}{R_g^2} \int_0^1 ds \left(\frac{d\mathbf{R}_{mn}}{ds}\right)^2 + U[\{\hat{\Phi}_\alpha\}] \right\}, \tag{1}$$

where $R_g = b\sqrt{N/6}$ is the radius of gyration of one strand. After integrating out the cross-link degrees of freedom, we recover the partition function of the classical Deam-Edwards theory for networks [45–48]. In the present approach, it will prove convenient to keep the cross-link degrees of freedom explicitly.

We first derive a mean-field approximation for the contributions of monomer interactions to the free energy in a standard field-theoretic SCF manner [3]: The chain conformations are decoupled by inserting identity operators $1 \propto \int_\infty \mathcal{D}\Phi_\alpha \int_{i\infty} \mathcal{D}W_\alpha e^{C\int d\mathbf{r} W_\alpha(\Phi_\alpha - \hat{\Phi}_\alpha)}$, where $\int_\infty \mathcal{D}\Phi_\alpha$ and $\int_{i\infty} \mathcal{D}W_\alpha$ denote functional integrals over fluctuating fields $\Phi_\alpha(\mathbf{r})$ and $W_\alpha(\mathbf{r})$. This allows us to rewrite the partition function in the form $\mathcal{Z} \propto \prod_\alpha \int_\infty \mathcal{D}\Phi_\alpha \int_{i\infty} \mathcal{D}W_\alpha \prod_l \int d\mathbf{r}_l e^{-\mathcal{F}[\{\Phi_\alpha, W_\alpha, \mathbf{r}_l\}]}$, with

$$\mathcal{F} = U[\{\Phi_\alpha\}] - C\sum_\alpha \int d\mathbf{r}\, \Phi_\alpha W_\alpha - \sum_{\langle jk \rangle} \ln \mathcal{Q}_{jk}(\mathbf{r}_j, \mathbf{r}_k). \tag{2}$$

Here the $\mathcal{Q}_{jk}(\mathbf{r}, \mathbf{r}')$ are single-chain partition functions of the linker strands $\mathbf{R}_{jk}(s)$ in the self-consistent field W_α, subject to the constraint that the ends are located at the cross-link positions $\mathbf{r}$ and $\mathbf{r}'$:

$$\mathcal{Q}_{jk}(\mathbf{r}, \mathbf{r}') = \int \mathcal{D}\mathbf{R} \Big|_{\substack{\mathbf{R}(0)=\mathbf{r} \\ \mathbf{R}(1)=\mathbf{r}'}} e^{-\int_0^1 ds\, \eta_{jk}^{(\alpha)}(s) W_\alpha(\mathbf{R}(s))}. \tag{3}$$

The SCF approximation consists of replacing the fluctuating field integral by its saddle point; i.e., the free energy is approximated by the minimum of $\mathcal{F}$ in Eq. (2) with respect to the fields Φ_α and W_α. One obtains the set of self-consistent SCF equations $CW_\alpha(\mathbf{r}) = \delta U/\delta\Phi_\alpha(\mathbf{r})$ and $\Phi_\alpha(\mathbf{r}) = \sum_{\langle jk \rangle} \delta \ln[\mathcal{Q}_{jk}(\mathbf{r}_j, \mathbf{r}_k)]/\delta W_\alpha(\mathbf{r})$. Efficient strategies to evaluate $\mathcal{Q}_{jk}$ and Φ_α can be found in the literature [5].

The remaining task is to find a corresponding mean-field approximation for the integration over the *cross-link* degrees of freedom. This is done following an analogous field-theoretic procedure. We define local cross-link distribution operators $\hat{p}_j(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}_j)$ and insert identities $1 \propto \int_\infty \mathcal{D}p_j \int_{i\infty} \mathcal{D}h_j e^{\int d\mathbf{r} h_j(p_j - \hat{p}_j)}$. The partition function is thus rewritten as $\mathcal{Z} \propto \prod_j \int_\infty \mathcal{D}p_j \int_{i\infty} \mathcal{D}h_j e^{-F[p_j, h_j]}$ with the new free energy functional

$$\begin{aligned} F = {} & U[\{\Phi_\alpha\}] - C\sum_\alpha \int d\mathbf{r}\, \Phi_\alpha W_\alpha \\ & - \sum_{\langle ij \rangle} \iint d\mathbf{r}\, d\mathbf{r}'\, p_j(\mathbf{r}) p_k(\mathbf{r}') \ln \mathcal{Q}_{jk}(\mathbf{r}, \mathbf{r}') \\ & - \sum_l \int d\mathbf{r}\, h_l(\mathbf{r}) p_l(\mathbf{r}) - \sum_l \ln(\mathcal{N}_l), \end{aligned} \tag{4}$$

with $\mathcal{N}_l = \int d\mathbf{r} e^{-h_l(\mathbf{r})}$. The mean-field approximation then again consists of carrying out a saddle point integration, i.e., minimizing F in Eq. (4) with respect to p_j and h_j. This results in the mean-field equations

$$h_j(\mathbf{r}) = -\sum_{\{k\}_j} \int d\mathbf{r}'\, p_k(\mathbf{r}') \ln[\mathcal{Q}_{jk}(\mathbf{r}, \mathbf{r}')] \tag{5}$$

$$p_j(\mathbf{r}) = \mathcal{N}_j^{-1} e^{-h_j(\mathbf{r})}, \tag{6}$$

where the sum $\sum_{\{k\}_j}$ runs over the cross-links k that are directly linked with j.

As a side note, we remark that the free energy expression in Eq. (2) has the structure of a Hamiltonian for a lattice model with sites j, continuous degrees of freedom $\mathbf{r}_j$, and "interactions" $\ln \mathcal{Q}_{jk}$. Thus, mean-field methods developed for lattice models can be applied in the present problem as well. The approximation derived above is equivalent to the popular Bragg-Williams approximation [49] in a version for continuous degrees of freedom. It yields the same equations, (4)–(6). Other more sophisticated approximations such as the Bethe approximation [49] can be adopted as well. More details are found in the Supplemental Material [50]. Unless stated otherwise, we will use Eqs. (4)–(6) here, i.e., the Bragg-Williams approximation.

In the absence of any monomer interactions (phantom networks), the mean-field equations (5) and (6) can be solved analytically. For regular networks with equivalent cross-links, the cross-links are centered about their respective mean position $\mathbf{R}_j$ with a Gaussian distribution,

$$p_j(\mathbf{r}) = R_g^{-d}\sqrt{\frac{f}{4\pi}}^{d} \exp\left[-\frac{f}{4R_g^2}(\mathbf{r}-\mathbf{R}_j)^2\right], \tag{7}$$

where f is the functionality of the cross-link and d the spatial dimension. Thus the theory reproduces the phenomenon of cross-link localization on a scale of R_g, in agreement with theories of the sol-gel transition in networks [46–48].

Interacting networks swell due to the excluded volume interactions. As a result, the mean cross-link positions $\mathbf{R}_j$ move apart. In incompressible materials, however, the *shape* of the cross-link distribution is barely affected by the swelling. Figure 1 shows numerical results for an interacting network with square topology in two dimensions (2D) [51] in the Bragg-Williams and the Bethe approximation (equations are given in the Supplemental Material [50]). The Bragg-Williams result is practically indistinguishable from the prediction of Eq. (7).

Likewise, the cross-link distribution does not change if the network is deformed elastically. Figure 2(c) (top panel) shows the cross-link distribution for an (almost) incompressible homopolymer network that has been stretched considerably in one direction. It can be described almost perfectly by Eq. (7). Specifically, we consider the network "unit cell" sketched in Fig. 2 with side length l_z. In the mechanically relaxed state, l_z takes the equilibrium value $l_z = l^* = 2/\sqrt{C}$. If the cells are stretched to $l_z \gg l^*$, the free energy per strand as a function of l_z rises quadratically according to $F/n_{\text{strands}} \approx l_z^2/(16R_g^2)$ [see Fig. 2(b), case $\chi N = 0$], which corresponds to the behavior of phantom networks of Gaussian chains. Incompressible homopolymer networks behave very much like phantom networks. Deviations only start to set in for strongly swollen networks with strand densities C below a crossover value $C^* = R_g^{-d}$ (with the spatial dimension d), which is the network equivalent of the overlap concentration in polymer solutions [52].

This changes in networks of AB copolymers. We consider the same (2D) square network as above [51], now made of AB diblock copolymers which are end-linked such that A ends join A and B ends join B [Fig. 2(a)]. By stretching the network in the z direction, an average distance $l_z/2$ is imposed between neighboring A and B cross-links, which induces a separation between A-rich and B-rich regions [Fig. 2(c)]. At $\chi N = 0$, the free energy rises monotonically as a function of l_z as discussed above (homopolymer case). As χN is increased, a minimum at nonzero l_z develops and gradually deepens [Fig. 2(b)]. This minimum dominates beyond $\chi N = 10.235$, and the network undergoes an order-disorder transition from a disordered state (with $l_z = l^* \ll R_g$) to a microphase separated lamellar state with lamellar spacing $l_z = 3.245R_g$. Compared to the noninteracting stretched structure at the same l_z, the stable lamellar state at the ODT is characterized by higher segregation, and by a narrower, more localized cross-link distribution.

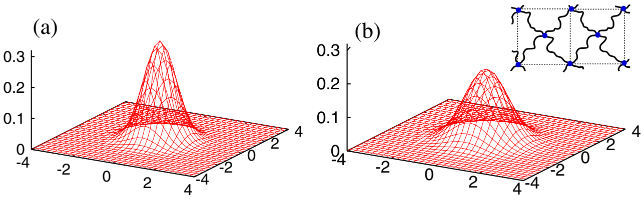

FIG. 1 (color online). Distribution of individual cross-links about their average position in a 2D melt of almost incompressible end-linked homopolymers ($\kappa N = 100$) at polymer density $CR_g^2 = 4$, calculated within the Bragg-Williams approximation (a) and the Bethe approximation (b). The network has the topology of a square lattice [see inset in (b)]. The distribution in (a) is indistinguishable from Eq. (7) with $f = 4$ and $d = 2$.

Comparing the ODT in the network to the ODT in copolymer melts, one notices striking dissimilarities. First, the transition is strongly first order already at the mean-field level. Second, stretching the system stabilizes the ordered phase. Free energy curves such as those shown in Fig. 2(b) can be used to construct a phase diagram as a function of the average force F_z acting on a strand. The result is shown in Fig. 3. As the system is stretched, the first order transition gradually moves to lower χN until it finally ends in a critical point at $(\chi N)_c = 3$. The critical point in the network is thus found at much lower χN than the critical point in the melt [$(\chi N)_c = 10.425$]. However,

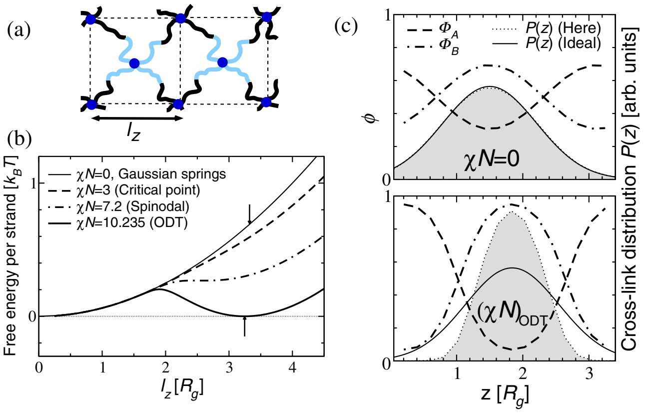

FIG. 2 (color online). Properties of a stretched AB diblock copolymer network in the 2D square topology sketched in (a) at $\kappa N = 100$ and strand density $CR_g^2 \to \infty$. The case $\chi N = 0$ also describes homopolymer networks. (b) Free energy per strand versus imposed cell length l_z for different values of χN as indicated. Arrows mark $l_z = 3.245R_g$. (c) Composition profile ($\Phi_{A,B}$: dashed and dot-dashed lines) and cross-link distribution profile (P: dotted and shaded curve) in arbitrary units across a lamella at imposed cell length $l_z = 3.245R_g$ for $\chi N = 0$ (top) and $\chi N = 10.235$ (bottom). For comparison, thin solid line shows cross-link distribution for nonstretched ideal (phantom) chains [Eq. (7)].

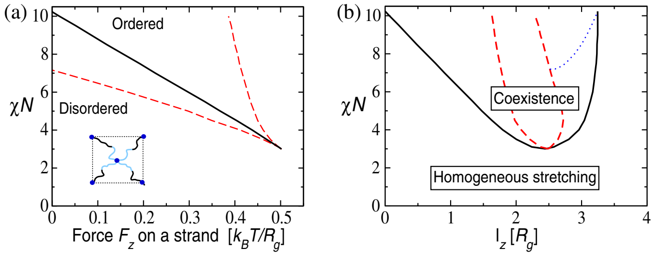

FIG. 3 (color online). Phase diagram for the system of Fig. 2 in the plane of χN versus (a) the average force acting on a strand F_z and (b) the imposed cell length l_z. Solid lines: coexistence. Dashed lines: spinodals. Dotted line in (b): lamellar distance l_z of (metastable or stable) ordered state in the stress-free system.

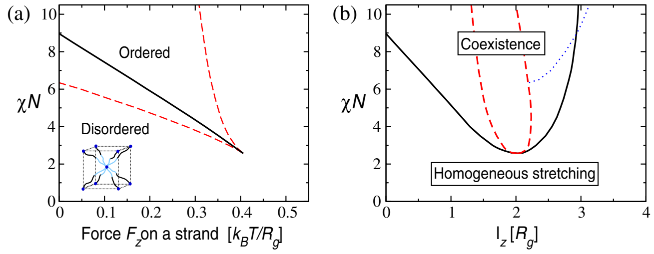

FIG. 4 (color online). Same as Fig. 3 for a three-dimensional network with a bcc topology [see inset in (a)].

the ODT in the stress-free system (at $F_z = 0$) is only slightly shifted compared to the melt.

The exact value of the ODT depends on the network topology and on the spatial dimension. For comparison, we have also calculated the phase behavior for a three-dimensional network with bcc topology (Fig. 4). The resulting phase diagram is similar to the two-dimensional one. The shift of the ODT is more pronounced, but still not spectacular. Thus, we find that weak cross-linking does not stabilize lamellar order efficiently, in agreement with the simulation results of Lay *et al.* [41].

Finally, we discuss the elastic behavior of the network. We focus on the three-dimensional case and calculate Young's moduli for our bcc topology. In the isotropic disordered state, the modulus is given by $B_i = 1.5C^{1/3}/R_g^2$, indicating that the network becomes stiff at high strand density C. In the ordered state, the modulus depends on the direction of applied stress. The elastic response to stretching in the direction normal to the lamellae is stiffer than in the isotropic case, $B_n = 2.12C$. In contrast, the system is soft in the parallel directions, with a modulus that does not depend on C at all, $B_\parallel = 1.36/R_g^2$. Hence, the elastic penalty for stretching lamellae in plane is found to be much smaller than the penalty for stretching them in the normal direction. This is compatible with a prediction of Panyukov and Rubinstein [39] based on a phenomenological model for networks. On applying stress to a microphase separated system with initially randomly oriented lamellae, one thus expects the lamellae to be kinetically driven towards aligning parallel to the applied stress. This was indeed observed experimentally [53]. The true state of lowest free energy, however, is one where the lamellae are oriented normal to the stress, such that the (elongated) copolymer strands are aligned parallel to the applied force. Lamellae with parallel orientation can only reach this state by copolymer reordering, which involves crossing an energy barrier. Hence the parallel orientation might be stabilized kinetically in many cases, even though the true equilibrium state is one with normal orientation.

To summarize, we have presented a way to extend the SCF theory to quenched polymer networks. It opens up a wide range of new applications for the SCF approach, such as the study of chemically or physically cross-linked systems, or of liquid crystalline elastomers (using suitable extensions of the SCF theory [14]). We have used the approach to study the ODT in networks of diblock copolymers, and the results were compatible with available simulations, experiments, and phenomenological theories.

In this Letter, the theory was developed for regular networks. The next step in future work will be to include disorder, and disorder averages, e.g., within a coherent potential approximation type approach. In this context, it will be interesting to establish the connection to classical field theories of networks based on the Deam-Edwards approach [45–47], which focus on the process of generating topological disorder during cross-linking. Another important issue is the effect of entanglements. The present theory ignores topological interactions by construction (since the monomers have no hard-core interactions). However, the effect of entanglements may be similar to that of physical cross-links, e.g., in interpenetrating networks [54–56], and it might be possible to treat them as effective cross-links in some cases.

The present theory can also be used as a starting point for simpler Landau-type expansions. For example, the derivation of a random phase approximation theory [57] for networks might give additional insight into the nature of the phase transitions in the system.

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