Self-Consistent Field Approach for Crosslinked Copolymer Materials

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A generalized self-consistent field approach for polymer networks with fixed topology is developed. It is shown that the theory reproduces the localization of crosslinks which is characteristic for gels. The theory is then used to study the order-disorder transition in regular networks of endlinked diblock copolymers. Compared to diblock copolymer melts, the transition is shifted towards lower values of the incompatibility parameter $\chi$ (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 \cite{1,2} is a powerful mean field approach for describing inhomogeneous polymer melts and solutions. Originally developed as a theory for interfaces between immiscible homopolymer phases \cite{3}, it has by now become a standard tool for studying phase transitions between block copolymer mesophases \cite{4,5}, the self-organization of amphiphilic polymers in solution \cite{6,7}, or the structure of polymer composite materials \cite{8,9}, to name just a few examples. Numerous extensions have been proposed that allow one to include, e.g., orientational order \cite{10}, electrostatic interactions \cite{11}, dynamical processes \cite{12,13,14} or the effect of fluctuations \cite{15,16,17,18}.

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 \cite{19,20}. 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 \cite{21,22,23}. Whereas this is all well understood in polymer melts, the situation in crosslinked systems is less clear.

Most theoretical studies of microphase separation in crosslinked polymer blends have focussed on situations where a blend of incompatible A and B polymers is first randomly crosslinked 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 \cite{24}. Several authors have built on this idea and investigated the instability by experiment \cite{25}, theory \cite{26,27,28,29,30} and simulation \cite{31,32}. The influence of random network forces on the structure of the ordered state was investigated by elasticity theories \cite{33,34,35}.

Here, we will consider a slightly different situation: We will study a diblock copolymer network crosslinked in a lamellar state, asking whether and how crosslinking stabilizes the lamellar structure. In computer simulations, Lay et al. \cite{36} found that the lamellar order of loosely crosslinked ordered diblock copolymer melts disappears upon heating. We will investigate this phenomenon. More specifically, we will consider a regular network of endlinked diblock copolymers. Experimentally, the synthesis of such ideal copolymer networks is coming within reach \cite{37,38}, and simple phenomenological theories have been devised to predict the expected microphase separation \cite{39,40,41,42,43,44,45}. 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 crosslinks $l$ and linker connections $(jk)$, (ii) the crosslink positions $r_j$ and the conformations of linker strands, which we parameterize by space curves $R_{jk}(s)$ with $s \in [0,1]$, and (iii) the sequence of monomers along the strands, described by characteristic functions $\eta^\alpha_{jk}(s)$, with $\eta^\alpha_{jk}(s) = 1$ if the chain is occupied by monomers of type $\alpha$ at the position $s$, and $\eta^\alpha_{jk}(s) = 0$ otherwise ($\sum_{\alpha} \eta^\alpha_{jk}(s) = 1$). 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 $Q_{jk}$. Here the $Q_{jk}$ allows us to rewrite the partition function in the form $Z \propto \sum_{\alpha} \prod_j \int_0^1 ds \, \delta(r - R_{jk}(s)) \, \eta^\alpha_{jk}(s)$, where $\chi$ is the Flory-Huggins parameter and $\kappa$ is related to the inverse compressibility of the melt. Here and in the following, the energy units are chosen such that $k_BT = 1$.

The partition function of the whole system thus reads

$$Z = \prod_i \int \prod_{<jk>} dR_{jk} \, \delta(r_j - R_{jk}(0)) \, \delta(r_k - R_{jk}(1)) \times \exp \left( - \sum_{<mm>} \frac{1}{R_g^2} \int_0^1 ds \left( \frac{dR_{mm}}{ds} \right)^2 + U(\{\Phi_{\alpha}\}) \right),$$

where $R_g = b\sqrt{N/6}$ is the radius of gyration of one strand. After integrating out the crosslink degrees of freedom, we recover the partition function of the classical Deam-Edwards theory for networks [50]. In the present approach, it will prove convenient to keep the crosslink 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 $1 \propto \int R_{jk} d\Phi_{\alpha} \int_0^1 dW_{\alpha} \, e^{C \int dW_{\alpha} (\Phi_{\alpha} - \phi_{\alpha})}$, where $\int d\Phi_{\alpha}$ and $\int dW_{\alpha}$ denote functional integrals over fluctuating fields $\Phi_{\alpha}(r)$ and $W_{\alpha}(r)$. This allows us to rewrite the partition function in the form

$$F = U(\{\Phi_{\alpha}\}) - C \sum_{\alpha} \int d\Phi_{\alpha} W_{\alpha} - \sum_{<jk>} \ln Q_{jk}(r_j, r_k).$$

(2)

Here the $Q_{jk}(r, r')$ are single-chain partition functions of the linker strands $R_{jk}(s)$ in the self-consistent field $W_{\alpha}$, subject to the constraint that the ends are located at the crosslink positions $r$ and $r'$:

$$Q_{jk}(r, r') = \int DR \bigg|_{R(0)=r} e^{-\int_0^1 ds \eta^\alpha_{jk}(s) W_{\alpha}(R(s))}.$$

(3)

The SCF approximation consists in replacing the fluctuating field integral by its saddle point, i.e., the free energy is approximated by the minimum of $F$ in Eq. (2) with respect to the fields $\Phi_{\alpha}$ and $W_{\alpha}$. One obtains the set of self-consistent SCF equations $CW_{\alpha}(r) = \delta U/\delta \phi_{\alpha}(r)$ and $\Phi_{\alpha}(r) = \sum_{<jk>} \delta \ln(Q_{jk}(r_j, r_k))/\delta W_{\alpha}(r)$. Efficient strategies to evaluate $Q_{jk}$ and $\Phi_{\alpha}$ can be found in the literature [3].

The remaining task is to find a corresponding mean-field approximation for the integration over the crosslink degrees of freedom. This is done following an analogous field-theoretic procedure. We define local crosslink distribution operators $p_j(r) = \delta(r - r_j)$ and insert identities $1 \propto \int \int \int_h \int R_{jk} e^{\int dr_{jk} h_{jk}(p_j - p_{j})}$. The partition function is thus rewritten as $Z \propto \prod_j \int_0^1 dR_{jk} \int_0^1 dh_{jk} \, e^{-\int [p_j, h_{jk}]}$ with the new free energy functional

$$F = U(\{\Phi_{\alpha}\}) - C \sum_{\alpha} \int d\Phi_{\alpha} W_{\alpha} - \sum_{<ij>} \int d\Phi_{\alpha} \int d\Phi_{\alpha'} \, p_j(r_j) \, p_k(r_k) \ln Q_{jk}(r_j, r_k')$$

$$- \sum_{l} \int dh_l(p_l) \, p_l(r_l) - \sum_{l} \ln(N_l)$$

(4)

with $N_l = \int dr \, e^{-h_l(r)}$. The mean-field approximation then again consists in 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

$$h_j(r) = - \sum_{\{k\}} \int dr' \, p_k(r') \ln(Q_{jk}(r, r'))$$

(5)

$$p_j(r) = N_{j}^{-1} e^{-h_j(r)},$$

(6)

where the sum $\sum_{\{k\}}$ runs over the crosslinks $k$ 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 $r_j$, and “interactions” $\ln Q_{jk}$. 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 [50] in a version for continuous degrees of freedom. It yields the same equations, [46]. Other more sophisticated approximations such as the Bethe approximation [50] can be adopted as well. More details are found in the supplemental information. 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 (4) and (5) can be solved analytically. For regular networks with equivalent crosslinks, the crosslinks are centered about their respective mean position $R_j$ with a Gaussian distribution,

$$p_j(r) = R^{-d}_g \sqrt{\frac{4\pi}{d}} \exp(-\frac{4}{R^2} (r - R_j)^2).$$

(7)
where \( f \) is the functionality of the crosslink and \( d \) the spatial dimension. Thus the theory reproduces the phenomenon of crosslink localization on a scale of \( R_g \), in agreement with theories of the sol-gel transition in networks \( 48 \).

Interacting networks swell due to the excluded volume interactions. As a result, the mean crosslink positions \( \mathbf{R}_j \) move apart. In incompressible materials, however, the shape of the crosslink distribution is barely affected by the swelling. Fig. 1 shows numerical results for an interacting network with square topology in two dimensions (2D) \( \mathbb{Z}^2 \) in the Bragg-Williams and the Bethe approximation (equations are given in the supplemental information). The Bragg-Williams result is practically indistinguishable from the prediction of Eq. 7.

Likewise, the crosslink distribution does not change if the network is deformed elastically. Fig. 2(c) (top panel) shows the crosslink 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 \( l_z > l^* \), 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. 2b), 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 \( 51 \).

This changes in networks of AB copolymers. We consider the same (2D) square network as above \( \mathbb{Z}^2 \), now made of AB diblock copolymers which are endlinked such that A ends join A and B ends join B (Fig. 2a). By stretching the network in the \( z \) direction, an average distance \( l_z/2 \) is imposed between neighboring A and B crosslinks, which induces a separation between A rich and B rich regions (Fig. 2c). At \( \chi N = 0 \), the free energy rises monotonically as a function of \( l_z \) as discussed above (homopolymer case). As \( \chi N \) is increased, a minimum at nonzero \( l_z \) develops and gradually deepens (Fig. 2b). This minimum dominates beyond \( \chi N = 10.235 \), and the network undergoes an order-disorder transition (ODT) 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 same \( l_z \), the stable lamellar state at the ODT is characterized by higher segregation, and by a narrower, more localized crosslink distribution.

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 \( \chi N \) 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 \( \chi N \) than the critical point in the melt \( (\chi N)_{c} = 10.425 \). However, 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...
FIG. 3: Phase diagram for the system of Fig. 2 in the plane of $\chi_N$ vs. (a) the average force acting on a strand $F_0$, (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.

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 $B_i = 1.5C^{1/3}/R^2$, 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, $B_\parallel = 1.36/R^2$. 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 [41] 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 [52]. 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 crosslinked 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 the present paper, 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 CPA (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 [46-48], which focus on the process of generating topological disorder during crosslinking. Another important issue is the effect of entanglements. The present theory ignores topological interactions by construction (since the monomers have no hardcore interactions). However, the effect of entanglements may be similar to that of physical crosslinks, e.g., in interpenetrating networks [53,55], and it might be possible to treat them as effective crosslinks 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 RPA (Random Phase Approximation) theory [56] for networks might give additional insight into the nature of the phase transitions in the system.

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Supplemental information

In the following, we give and motivate the mean-field equations for polymer crosslink distributions in the Bethe approximation, which were used to obtain Fig. 1 (b). To put the Bethe approximation into context, we begin with giving an alternative derivation of the Bragg-Williams equations, Eqs. (4-6), which does not rely on field theory, but adopts a more traditional approach. The starting point is Eq. (2), which defines an "effective Hamiltonian" of the form

$$ F = F_0 - \sum_{<jk>} \ln Q_{jk}(\mathbf{r}_j, \mathbf{r}_k), \quad (8) $$

where the sum $<jk>$ runs over connected neighbors and $F_0$ does not depend explicitly on the crosslink positions $\mathbf{r}_j$. (It does of course depend implicitly on the crosslink positions, once the self-consistent solution for the densities $\Phi$ and fields $W$ has been inserted, but here we may take $\Phi$ and $W$ to be fixed).

The free energy of the system is given by

$$ F = \langle F \rangle - S, \quad (9) $$

with the average energy $\langle F \rangle$ and the entropy $S$. As before, the temperature has been set to one. Our task is to evaluate and minimize this expression with respect to the global distribution function of the $M$ crosslinks in the system, $P(\mathbf{r}_1, \ldots, \mathbf{r}_M)$.
In the Bragg-Williams approximation, one assumes that the global distribution function factorizes, \( P(r_1, \cdots, r_m) = \prod_i p_i(r_i) \). Inserting this gives the average energy

\[
\langle F \rangle_{BW} \approx \mathcal{F}_0 - \sum_{<jk>} \int \int dr \, dr' \, p_j(r) \, p_k(r') \, \ln Q_{jk}(r, r') \tag{10}
\]

and the entropy of the crosslink distribution

\[
S_{BW} \approx - \sum_l \int dr \, p_l(r) \, \ln(p_l(r)) \tag{11}
\]

The minimization of Eq. (9) with respect to the functions \( p_l(r) \) under the constraint \( \int dr \, p_l(r) = 1 \) for all \( l \) results in Eqs. (5) and (6), and the free energy (4).

Whereas all correlations between crosslinks are neglected in the Bragg-Williams approximation, the Bethe approximation accounts for correlations between crosslinks that are directly connected (i.e., that have direct interactions with each other). Hence the factorization approximation is dropped for these pairs, and the global distribution function is approximated by

\[
P(r_1, \cdots, r_M) = \prod_{<jk>} p_{jk}^{(2)}(r_j, r_k) / \prod_l [p_l(r_l)]^{c_l-1}, \tag{12}
\]

where \( p_{jk}^{(2)} \) are the pair distribution functions, and \( c_l \) is the connectivity of crosslink \( l \). We note that \( p_{mn}(r_m, r_n)/p_n(r_n) \) is the conditional probability of finding the crosslink \( m \) at position \( r_m \), if crosslink \( n \) is at position \( r_n \). Using this relation, one can easily check that the approximation (12) fulfills \( \prod_{l \neq (j,k)} \int dr \, P(r_1, \cdots, r_m) = p_{jk}^{(2)}(r_j, r_k) \). The approximation (12) results in the expression (11) for the energy, and

\[
\mathcal{F}_{\text{Bethe}} \approx \mathcal{F}_0 - \sum_{<jk>} \int \int dr \, dr' \, p_{jk}^{(2)}(r, r') \, \ln(p_{jk}^{(2)}(r, r')) + \sum_l (c_l - 1) \int dr \, p_l(r) \, \ln(p_l(r)) \tag{14}
\]

for the entropy. After minimizing again Eq. (9) with respect to \( p_{jk}^{(2)} \) and \( p_l \), subject to the constraints \( \int dr \, p_{jk}^{(2)}(r, r') = p_k(r') \), \( \int dr' \, p_{jk}^{(2)}(r, r') = p_j(r) \), and \( \int dr \, p_l(r) = 1 \), we finally obtain the Bethe equations

\[
p_{jk}^{(2)}(r, r') = M_{jk}(r) Q_{jk}(r, r') \overline{M}_{jk}(r') \tag{15}\]

\[
p_l(r) = N_l \prod_{\{j\}} M_{jl}(r)^{1/(c_l-1)} \prod_{\{j'\}} \overline{M}_{j'l}(r)^{1/(c_l-1)}. \tag{16}\]

Here the products \( \prod_{\{j\}} \) and \( \prod_{\{j'\}} \) run over the connected neighbors of the crosslink \( l \), and the functions \( M_{jk}(r), \overline{M}_{jk}(r) \), as well as the constants \( N_l \) must be determined self-consistently such that the constraints are satisfied. The resulting free energy in Bethe approximation takes the simple form

\[
F_{\text{Bethe}} = \mathcal{F}_0 - \sum_l (c_l - 1) N_l. \tag{17}\]

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