Glassy correlations and microstructures in randomly crosslinked homopolymer blends

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We consider a microscopic model of a polymer blend that is prone to phase separation. Permanent crosslinks are introduced between randomly chosen pairs of monomers, drawn from the Deam-Edwards distribution. Thereby, not only density but also concentration fluctuations of the melt are frozen-in in the gel state, which emerges upon sufficient crosslinking. We derive a Landau expansion in terms of the order parameters for gelation and phase separation, and analyze it on the mean-field level, including Gaussian fluctuations. The mixed gel is characterized by thermal as well as time-persistent (glassy) concentration fluctuations. Whereas the former are independent of the preparation state, the latter reflect the concentration fluctuations at the instant of crosslinking, provided the mesh size is smaller than the correlation length of phase separation. The mixed gel becomes unstable to microphase separation upon lowering the temperature in the gel phase. Whereas the length scale of microscopic separation is given by the mesh size, at least close to the transition, the emergent microstructure depends on the composition and compressibility of the melt. Hexagonal structures, as well as lamellae or random structures with a unique wavelength, can be energetically favorable.

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I. INTRODUCTION

Crosslinked homopolymer blends exhibit a rich phase diagram, due to the competition between phase separation and crosslinking. The simplest case is of a blend of two homopolymer species, “A” and “B”, whose incompatibility is controlled by the Flory-Huggins parameter χ and which are crosslinked irreversibly by some number Nc of chemical bonds. In addition, the concentration fluctuations can be controlled independently in the process of crosslinking (preparation state) and the well crosslinked gel (measurement state), e.g. by lowering the temperature in the gel. Hence we have three control parameters: the incompatibility χp in the preparation state, the incompatibility χm in the measurement state, and the number of crosslinks per chain, μ = Nc/N, where N denotes the total number of chains in the melt.

A statistical mechanical theory thus has to include not only the average over the quenched disorder (crosslink realization) but also the “memory” of the preparation state. This can be achieved in the following way: We start from a microscopic model, which accounts for the repulsive interaction of all monomers, irrespective of species (excluded volume), as well as for a repulsive interaction between the different species only (incompatibility). Crosslinks are introduced between randomly-chosen pairs of monomers. The probability for a particular crosslink configuration depends on the preparation state of the system, such that monomers with a high probability to be close in the preparation state have a high probability to be crosslinked. Thereby the crosslinks indeed preserve the memory of the preparation state. Mathematically, this is achieved via the Deam-Edwards distribution and the replica trick to average over the quenched disorder.

We expect and indeed find signatures of the preparation state in the gel. An example are the concentration fluctuations which are frozen in by the crosslinks. If the preparation state is close to macroscopic phase separation then the glassy, i.e. time-persistent, concentration fluctuations reflect the correlations of the melt at the moment of crosslinking. If, on the other hand, the preparation state is far from phase separation then the frozen fluctuations are completely random and follow the pattern set by the crosslinks.

Lowering the temperature in the gel or, equivalently, increasing the incompatibility at measurement χm will ultimately give rise to microphase separation, while macroscopic demixing is suppressed by the crosslinks. A variety of microphases can exist, depending on the composition of the blend and its compressibility. If the mixture is symmetric, having equal concentrations of “A” and “B” monomers, then lamellae are energetically favorable, whereas for an asymmetric mixture hexagons prevail. A finite compressibility enhances the tendency towards phase separation and can induce a random pattern, consisting of a superposition of many lamellar phases of different orientation. In all cases the critical wave-number is given by the mesh size or localization length of the gel.

The subject of crosslinked homopolymer blends was first addressed by de Gennes, who pointed out that the mixed state is stabilized in the gel and eventually undergoes microphase separation. His predictions were verified experimentally with, however, a discrepancy in the scattering intensity for small wave-number.

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This was traced back to the neglect of concentration fluctuations which are present during crosslinking and are partially frozen in by the crosslinks. Subsequently several attempts were made to include these effects approximately [54, 55]. Studies of crosslinked systems, based on the microscopic model by Panyukov and Rabin [56], were reported by Sfatos and Shakhnovich [57]; as far as homopolymer blends are concerned, these authors recover de Gennes’ result within a microscopic approach. Computer simulations were carried out by Lay and Sommer [58] who studied, in particular, the relation of the domain sizes to the mesh size of the gel. In the last section of our paper we present a detailed discussion of the literature in comparison with our own results.

The paper is organized as follows: In sec. II we formulate a microscopic model of crosslinked polymer chains. Subsequently (sec. III) we derive a Landau expansion in terms of the order parameters for gelation and phase separation. The Landau theory allows us to discuss the mixed gel (sec. IV) as well as microphase separation (sec. V). We conclude with a short summary, a comparison with previous theoretical work and an outlook.

II. MODEL

A. Uncrosslinked homopolymer blend

We first consider an uncrosslinked blend of polymer, modeled as a system of Gaussian phantom chains of equal degree of polymerization $L$ and step length $b$. The melt is taken to contain $N_A$ chains of type A and $N_B$ chains of type B. In general, there will be an imbalance in concentration $q := (N_A - N_B)/N$ where $N = N_A + N_B$ is the total number of chains, occupying a volume $V$ in $d$-dimensional space. The monomers are denoted as $R_{a,i}(s)$, where $a = A, B$ refers to the chain species, $i = 1, \ldots, N_a$ enumerates the chains, and $s = 0 \ldots 1$ is the continuous index for a “site” on a chain. It turns out to be convenient to express the monomer positions by dimensionless vectors $r_{a,i}(s) = \sqrt{d/Lb^2} R_{a,i}(s)$, so that all lengths are measured in units of the radius of gyration of the free chains, $R_g = Lb^2/6$. The rescaled volume reads $V := (d/Lb^2)^{d/2} V$.

The chain connectivity is described by the usual Wiener Hamiltonian

$$H^W = \frac{k_B T}{2} \sum_{a=A,B} \sum_{i=1}^{N_a} \int_0^1 ds \left( \frac{dr_{a,i}(s)}{ds} \right)^2 ,$$

the excluded volume term controlling compressibility reads

$$H^\lambda = \frac{V}{4N} \sum_{a,a'=A,B} \sum_{i,i'=1}^{N_a} \int_0^1 ds \int_0^1 ds' \times \delta(r_{a,i}(s) - r_{a',i'}(s')) ,$$

and the incompatibility of the two monomer species is modeled by the interaction

$$H^\chi = -\frac{V}{4N} \sum_{a,a'=A,B} \sum_{i,j=1}^{N_a} \langle 2 \delta_{a,a'} - 1 \rangle \int_0^1 ds \int_0^1 ds' \times \delta(r_{a,i}(s) - r_{a',i'}(s')) .$$

Although the chain elasticity and the volume exclusion are of mainly entropic origin, the incompatibility is assumed to be a chiefly energetic contribution. Nevertheless we let $k_B T = 1$ in the following to simplify the expressions. Instead of changing the temperature, we shall tune $\lambda$ and particularly $\chi$, which will serve as the inverse temperature.

B. Crosslinking

Chemical crosslinking induces a random number $M$ of permanent bonds between randomly selected pairs of monomers; a particular realization of crosslinks is denoted by $C = \{(a_i, i, s_e, a'_i, i', s'_i)\}_{i=1}^{M}$. The links are modeled as hard constraints with zero bond length. The partition function of the crosslinked melt, relative to a melt of non-interacting chains, thus reads

$$Z(C) := \prod_{e=1}^{M} \delta (r_{a_i, i_e}(s_e) - r_{a'_i, i'_e}(s'_e)) \exp \{-H^\lambda - H^\chi\}^W$$

$$:= \int D\mathbf{r}_{a,i}(s) \prod_{e=1}^{M} \delta (r_{a_i, i_e}(s_e) - r_{a'_i, i'_e}(s'_e)) \exp \{-H^W - H^\lambda - H^\chi\} \int D\mathbf{r}_{a,i}(s) \exp \{-H^W\} .$$

Here we have implicitly defined the expectation value $\langle \ldots \rangle^W$ with respect to the Hamilton function of the uncrosslinked melt.
C. Disorder average and Deam-Edwards distribution

We are interested in the properties of the "generic" melt rather than in the properties of a melt with a specific set of crosslinks. Furthermore, we assume the system to be self-averaging in the thermodynamic limit. Therefore we will consider disorder averages of the observables with respect to the quenched randomness of crosslinks.

We specify the probability distribution of the crosslink sets following the strategy of Deam and Edwards [1]. We suppose that the dominant crosslink sets are those that are most compatible with the uncrosslinked melt. More precisely, we assume a probability distribution

\[ \mathbb{P}_M(C) \propto \left( \frac{\mu N/V}{M!} \right)^M Z_p(C). \] (5)

Here, \( Z_p \) is given by eq. (3), evaluated at \( \lambda = \lambda_p \) and \( \chi = \chi_p \), which characterize the system prior to crosslinking. Disorder averages with respect to \( \mathbb{P}_M \) will be denoted by square brackets.

D. Order parameters for the homopolymer blend

To discriminate between the liquid state and the amorphous solid state of the polymer system we use the order parameter proposed in [12]:

\[ \tilde{\Omega}_{k_1 \ldots k_g} := \frac{1}{N} \sum_{a=A,B} \sum_{i=1}^{N_a} \int_0^1 \text{d}s \left\{ \exp(ik_hr_{a,i}(s)) \right\}_C \times \ldots \times \left\{ \exp(ik_pr_{a,i}(s)) \right\}_C, \] (6)

for \( g = 1, 2, \ldots \) and nonzero \( \{k_i\} \). The symbol \( \left\{ \ldots \right\}_C \) denotes the thermal expectation value in the presence of a particular realization \( C \) of crosslinks. In the case \( g = 1 \), eq. (3) is the thermal average of the monomer density in Fourier space,

\[ \tilde{\rho}_k := \frac{1}{N} \sum_{a=A,B} \sum_{i=1}^{N_a} \int_0^1 \text{d}s e^{-ikr_{a,i}(s)}. \] (7)

In the liquid state, a monomer explores the sample volume uniformly. Hence, the equilibrium value of the local density is constant and the Fourier transform \( \langle \exp(ikr_i(s)) \rangle_C \) vanishes (except for \( k = 0 \), which we exclude). The order parameter (3) therefore is always zero in the liquid state.

In a solid, at least a finite fraction of the monomers are localized about points \( b_{a,i}(s) \) in space. For these monomers, \( \langle \exp(ikr_{a,i}(s)) \rangle_C \propto e^{ikb_{a,i}(s)} \neq 0 \). However for an amorphous, i.e. macroscopically translation-invariant (MTI) solid, the disorder averaged expectation value \( \langle \tilde{\Omega}_{k_1 \ldots k_g} \rangle_C \) vanishes unless \( k_1 + \cdots + k_g = 0 \), see [12].

In particular \( \langle \tilde{\rho}_k \rangle_C = 0 \) in the MTI state. Hence we can discriminate between the liquid and the amorphous solid state by means of the \( g \geq 2 \) values of eq. (3). (For the signature of crystalline and globular states, see [12]).

Throughout this article, we will also refer to the two monomer species as “opposite charges”. The identification of \( A_1 \)s and \( B_1 \)s with positive and negative charges, respectively, leads to a natural choice for an order parameter detecting phase separation: the “charge density”

\[ \tilde{\Psi}_k := \frac{1}{N} \sum_{i=1}^{N_A} \int_0^1 \text{d}s e^{-ikr_{A,i}(s)} - \frac{1}{N} \sum_{i=1}^{N_B} \int_0^1 \text{d}s e^{-ikr_{B,i}(s)} \] (8)

measuring the local imbalance of the concentrations of \( A \) and \( B \).

In the general case of an asymmetric blend, in which there is an excess of either \( A \)- or \( B \)-chains, the average charge density is given by \( q = N/V = (N_A - N_B)/V \), so that \( \tilde{\Psi}_k \) serves as an order parameter only for \( k \neq 0 \). Homogeneous phase separation is indicated by a nonzero expectation value of \( \langle \tilde{\Psi}_k \rangle_C \) at finite wave-number. A nonuniform charge density in general is accompanied by mass density modulations, except for the incompressible case.

In the gel phase we expect to find static charge fluctuations \( \langle \tilde{\Psi}_k \rangle_C \neq 0 \) for all wave-numbers. If the gel state is a homogeneous mixture of \( A \) and \( B \) chains then the disorder averaged charge density vanishes, i.e. \( \langle \tilde{\Psi}_k \rangle_C = 0 \). The frozen-in fluctuations can only be detected by the glassy correlations \( \langle \tilde{\Psi}_k \rangle_C \langle \tilde{\Psi}_{-k} \rangle_C \) In general, the quadratic expectation values \( \langle \tilde{\Psi}_k \tilde{\Psi}_{-k} \rangle_C \) and \( \langle \tilde{\Psi}_k \rangle_C \langle \tilde{\Psi}_{-k} \rangle_C \) measure volatile and time-persistent charge fluctuations in an an priori homogeneous mixture.

III. EFFECTIVE FREE ENERGY

The disorder averaged free energy

\[ F = -\ln \left[ \left. \mathbb{P}(Z) \right| \right] - \lim_{n \to 0} \left[ \left( \frac{Z}{n} \right) - 1 \right] \] (9)

is computed with help of the replica trick. The \( n \)-th power of \( Z \) is made explicit using \( n \) independent copies – replicas – of the system and an additional replica is introduced to account for the Dean-Edwards distribution [12]. The average over the disorder can be carried out explicitly, yet at the cost of a coupling between the formerly independent replicas, yielding

\[ [Z^n] = 0, \] (10)

where the replicated partition function is given by
Here, the $r^\alpha_{a,i}(s)$ denote the monomer positions in the $\alpha^{th}$ replica, $\langle \ldots \rangle_{n+1}^W$ is the replicated Wiener average, and $H_{n+1}^\lambda$ and $H_{n+1}^{\lambda+1}$ denote the replicated Hamiltonians of the excluded volume and incompatibility interactions. The denominator and the zeroth replica in the numerator are due to the Deed-Edwards distribution $\mathcal{P}$ and reflect the situation prior to crosslinking. Thus, we have to distinguish between the zeroth replica, characterized by $\lambda_0$ and $\chi_p$ (preparation ensemble), and the other $n$ replicas, reflecting the situation after crosslinking, characterized by $\lambda_m$ and $\chi_m$ (measurement ensemble). To account for the particular role of the zeroth replica we use the notation

$$
\lambda^\alpha := \begin{cases} 
\lambda_p & \text{if } \alpha = 0, \\
\lambda_m & \text{otherwise,}
\end{cases}
$$

(12)

$$
\chi^\alpha := \begin{cases} 
\chi_p & \text{if } \alpha = 0, \\
\chi_m & \text{otherwise.}
\end{cases}
$$

(13)

The many-particle problem of the polymer melt can be formally reduced to a two-chain problem (one chain of each species). It is convenient to introduce $(n+1)$-fold replicated vectors $\hat{x} := (\mathbf{x}, \ldots, \mathbf{x}^n)$, and to express the exponents in eq. (11) in Fourier space, which leads to terms quadratic in the monomer and charge densities. These can be linearized by means of Hubbard-Stratonovich transformations, yielding

$$
\mathcal{Z}_n = \mathcal{B}_n \cdot \int \mathcal{D}(\{\Psi, \Omega, \rho\}) \exp\{-n\mathcal{F}_n(\{\Psi, \Omega, \rho\})\}
$$

(14)

with a constant $\mathcal{B}_n = \exp\left\{\frac{N}{2}(-n\lambda_m + nq^2\chi_m + ((n+1)V^{-n} - 1)\mu)\right\} = 1 + O(n)$ and the effective free energy

$$
n \mathcal{F}_n(\{\Psi, \Omega, \rho\}) = \frac{N}{2} \sum_{a,k}^\prime \left( \frac{1}{\lambda^\alpha} \frac{q^2}{\chi^\alpha} \right) |\Psi_k^\alpha|^2 + \frac{1}{\lambda^\alpha} |\rho_k^\alpha|^2 + \frac{iq}{\chi^\alpha} (\rho_k^\alpha \Psi_k^\alpha + \rho_{\bar{k}}^\alpha \Psi_{\bar{k}}^\alpha) + \frac{NV^n}{2\mu} \sum_k |\Omega_k|^2 - N_A \ln z_+(\{\Psi, \Omega, \rho\}) - N_B \ln z_- (\{\Psi, \Omega, \rho\}),
$$

(15)

where

$$
z_{\pm}(\{\Psi, \Omega, \rho\}) := \exp\left\{ \sum_{\alpha, k}^\prime \left( -i\rho_k^\alpha - (q+1)|\Psi_k^\alpha|^2 \right) - V^{-n} \sum_k |\Omega_k|^2 \int_0^1 ds e^{ikr^\alpha(s)} + V^{-n} \sum_{\alpha, \bar{k}}^\prime |\Omega_{\bar{k}}|^2 \int_0^1 ds e^{i\bar{k}r^\alpha(s)} \right\}_{n+1}^W.
$$

(16)
the fields according to
\[ \langle \hat{\Psi}_k \rangle_c = \frac{1}{\lambda m} \lim_{n \to 0} \langle \Psi_k^0 \rangle_{n+1} \]
and
\[ \langle \hat{\rho}_k \rangle_c = \frac{1}{\lambda m} \lim_{n \to 0} \langle \rho_k^0 + iq \Psi_k \rangle_{n+1} \]
for \( k \neq 0 \) and \( \alpha \geq 1 \), and
\[ \langle \hat{\Omega}_{k_1 \ldots k_q} \rangle = \frac{1}{\mu} \lim_{n \to 0} \langle \Omega_{k_1 \ldots k_q} \rangle_{n+1} \]
for \( \hat{k} = (0, k_1, \ldots, k_q, 0, \ldots, 0) \) with \( q \geq 2 \).

In asymmetric blends, which have an excess of either \( A \) or \( B \) chains, the average charge density \( qN/V = (N_A - N_B)/V \) is non-zero. To simplify the Landau expansion of the free energy it is then advantageous to either work with the fluctuations \( \delta \Psi = \Psi - q \) of the charge density around its mean value or, alternatively, shift the monomer density, as is done here.

### IV. HOMOGENEOUSLY MIXED STATES

On the mean field level, we approximate the functional integral over \( \Omega, \rho \) and \( \Psi \) in (14) by using the saddle point method, i.e. by the value of the integrand at the point \((\bar{\Psi}, \bar{\rho}, \bar{\Omega})\) making the integrand stationary:

\[ Z_n \sim \text{const} \cdot e^{-F_n(\bar{\Psi}, \bar{\rho}, \bar{\Omega})} \tag{17} \]

where, by definition, \((\bar{\Psi}, \bar{\rho}, \bar{\Omega})\) satisfy the stationarity conditions

\[ \frac{\partial F_n}{\partial \Psi^\alpha_k} \bigg|_{\bar{\Psi}, \bar{\rho}, \bar{\Omega}} = 0, \quad \frac{\partial F_n}{\partial \rho_k} \bigg|_{\bar{\Psi}, \bar{\rho}, \bar{\Omega}} = 0, \quad \frac{\partial F_n}{\partial \Omega_k} \bigg|_{\bar{\Psi}, \bar{\rho}, \bar{\Omega}} = 0. \tag{18} \]

#### A. Homogeneously mixed liquid state

One solution of the stationarity conditions (18) is the trivial saddle point \( \bar{\Psi} = \bar{\rho} = \bar{\Omega} = 0 \), corresponding to the homogeneously mixed liquid state. To assess its stability we consider the Landau expansion to leading order around this point:

\[ 2\pi F_n(\{\Psi, \rho, \Omega\}) = \sum_{\alpha, k} \left( \frac{1}{\lambda^\alpha} + g_D(k^2) \right) |\rho_k^\alpha|^2 + \sum_k \left( \frac{1}{\mu} - g_D(k^2) \right) |\Omega_k|^2 \]

\[ + 2iq \sum_{\alpha, k} \frac{1}{\lambda^\alpha} \Omega^\alpha_k \Psi_k^\alpha + \sum_{\alpha, k} \left( \frac{1}{\lambda^\alpha} - \frac{q^2}{\lambda^\alpha} - (1 - q^2)g_D(k^2) \right) |\Psi_k^\alpha|^2 + \mathcal{O}(\Psi^2, \rho^2, \Omega^2), \tag{19} \]

where the Debye function \( g_D \) is defined in appendix B.1.

The stability limits of the homogenous liquid can be read off from the quadratic coefficients. As \( g_D(k^2) \) decreases monotonically from one to zero, stability against solidification and demixing require \( \mu < 1 \) and \( (\chi_p, \chi_m) < 1/(1 - q^2) \), respectively. Throughout this article, we assume that \( (\lambda_p, \lambda_m) > \mu \), i.e. that the excluded volume interaction is strong enough to prevent density instabilities (see above).

It should be noted that the condition \( (\chi_p, \chi_m) < 1/(1 - q^2) \) denote local stability limits only. In mean-field theory, the phase separation transition for symmetric blends is of second order, so the phase transition coincides with the limit of local stability. In asymmetric blends the transition is of first order. The loss of local stability, as given by the conditions above, then defines a spinodal, and the transition occurs at a lower value of \( \chi \). The location of the spinodal depends on the average charge \( q \), with a larger critical incompatibility (i.e. lower critical temperature) for more asymmetric mixtures.

The gelation of the homogeneous liquid, driven by increasing the crosslink concentration, and the microphase separation of the resulting gel, induced by cooling, will be addressed in the following sections.

#### B. Crosslinking in the homogeneously mixed state

In the liquid state, the polymer blend phase separates macroscopically beyond the demixing threshold. The subsequent gelation of such a macrophase-separated melt would result, apart from the interface, in just two pieces of gel having different compositions. It is more interesting to consider a gel prepared from a homogeneous melt to study phase separation in the gel phase. As we shall see below, such a gel shows glassy charge density patterns and, as anticipated, microphase separation instead of macroscopic demixing. Therefore, the discussion will be restricted to crosslinking in a homogeneously mixed blend, \( \chi_p < 1/(1 - q^2) \), including undercooled mixtures for \( q \neq 0 \).
Upon gelation, the saddle point $\tilde{\Omega}_k = 0$ will become unstable, making it necessary to complement the expansion (19) of the free energy with the third-order terms:

$$\frac{2\pi}{N} \mathcal{F}_n(\{\Psi, \rho, \Omega\}) = \sum_{\alpha, k} \left( \frac{1}{\omega} - (1 - q^2) g_D(k^2) \right) |\Psi_k^n|^2 + \sum_k \left( \frac{1}{\mu} - g_D(k^2) \right) |\Omega_k|^2$$

$$- \sum_{\alpha_1 \neq \alpha_2} \sum_{k_1, k_2} \rho \Omega^{\alpha_1}_{k_1} \delta_{p^{\alpha_1}, k_1} \delta_{p^{\alpha_2}, k_2} - \frac{1}{3} \sum_{k_1, k_2, k_3} \Omega_{k_1} \Omega_{k_2} \Omega_{k_3} \delta_{k_1 + k_2 + k_3, 0}. \quad (20)$$

The vertex functions of the cubic terms have been approximated by their zero wave-number values, the complete expressions being given in appendix B. This approximation is well justified, because the gelation transition is always continuous, so that the relevant length-scales are very large, compared with the scales of the microscopic correlations. Here, we have taken the limit of an incompressible melt, which is achieved by integrating out the density fluctuations on the Gaussian level and subsequently taking the limit $\lambda \to \infty$.

We first discuss a gel in the homogeneously mixed state $\tilde{\Psi}_k = 0$, assuming $\chi_m < 1/(1 - q^2)$. Following [12], we consider the order parameter hypothesis

$$\tilde{\Omega}_k = \delta_{k,0} \cdot Q \int_0^\infty d\tau \rho(\tau) \exp(-\tilde{k}^2/2\tau) \quad (21)$$

with the shorthand $\tilde{k} := \sum_{\alpha=0}^n k^\alpha$. Here, $Q$ denotes the fraction of chains that are localized, i.e. the gel fraction; the localization lengths are distributed according to the distribution function $\rho(\tau)$. Both have to be determined self-consistently as a solution of the stationarity conditions [12].

The first two of the stationarity conditions are satisfied for any $Q$ and $\rho(\tau)$. The third condition is independent of the incompatibility parameter. Hence, in the homogeneously mixed regime, the task of determining $Q$ and $\rho(\tau)$ on the saddle-point level is exactly the same as in the pure gelation problem in [12]. In the present notation, the result for the solid state, i.e. $\mu > 1$, reads

$$\tilde{\Omega}_k \approx \delta_{k,0} \cdot 2\mu(\mu - 1) \cdot \omega \left( \frac{2}{\mu - 1} \right)$$

$$= \delta_{k,0} \cdot \mu(\mu - 1) \cdot w \left( \tilde{k}^2/(2\mu - 1) \right), \quad (22)$$

with the gel fraction approximately given by $Q \approx 2(\mu - 1)$. In the liquid state, $\tilde{\Omega}_k = 0$ and $Q = 0$. The scaling function $\omega(x)$ is defined in [12] (see appendix C for details); for convenience we define the shorthand $w(x) := \omega \left( \sqrt{8x/3} \right)$.

### C. Stability of the homogeneously mixed gel

Starting from a gel prepared from a homogeneous melt, i.e. $\chi_p < 1/(1 - q^2)$, we now allow the incompatibility to be changed after crosslinking. In order to keep the gel homogeneous, $\chi_m$ must remain smaller than the critical value $\chi_{\text{crit}}$ for (micro-)phase separation. As can be seen from the term coupling $\Psi_k$ and $\Omega_k$ in the effective free energy [20], the gel network stabilizes the mixed state; the details are discussed in the following.

As long as the gel is homogeneous, the order parameter [22] solves the stationarity conditions [12]. To determine the stability of the mixed state, we need the second derivative of $\mathcal{F}_n$ with respect to the charge density, evaluated at the saddle point. We restrict the discussion to a weak gel, i.e. $\mu - 1 \ll 1$, so that the saddle point value of $\tilde{\Omega}_k$ is small and the Hessian can be approximated by its expansion to linear order in $\Omega_k$. It then can be read off from the Landau expansion [20] with $\tilde{\Omega}_k$ replaced by the explicit saddle point value [22]. The latter vanishes unless $\tilde{k} = 0$: hence there is no coupling between the different $k$’s, and the Hessian can be calculated independently for each wave-vector. We obtain

$$\frac{\partial^2 \mathcal{F}_n}{\partial \Psi_k^n \partial \Psi_k^{n'}} \bigg|_{\tilde{\Psi}, \tilde{\Omega}} \approx N(1 - q^2) \cdot A_{\alpha_1 \alpha_2}(k), \quad (23)$$

where

$$A_{\alpha_1 \alpha_2} := \begin{pmatrix} c & -b & \ldots & -b \\ -b & a & \ddots & \vdots \\ \vdots & \ddots & \ddots & -b \\ -b & \ldots & \ldots & a \end{pmatrix} \quad (24)$$

with

$$a := \left( \frac{1}{(1 - q^2)\chi_m} - g_D(k^2) \right),$$

$$b := \mu(\mu - 1) w(k^2/(\mu - 1)), \quad \text{and}$$

$$c := \left( \frac{1}{(1 - q^2)\chi_p} - g_D(k^2) \right). \quad (25)$$

The stability of the homogeneous state is equivalent to the positivity of $A$. In the limit $n \to 0$, its eigenvalues
are given by
\[
\lambda_1(k) := c \quad \text{(non-degenerate), and} \quad \lambda_2(k) := a + b \quad \text{(n-fold degenerate).} \quad (26)
\]

As we assume crosslinking in the mixed phase, \( \lambda_1 \) is always positive, and thus the stability condition reduces to \( \lambda_2 > 0 \) or, equivalently \( \chi_m < \chi_{\text{crit}}(\mu) \) with
\[
(1 - q^2)\chi_{\text{crit}}(\mu) := \left(1/\max_k \left\{ g_D(k^2) - \mu(\mu - 1) w(k^2)/(\mu - 1)\right\}\right). \quad (28)
\]

Figure 1 shows \( \lambda_2(k) \) for \( \chi_m = 1/(1 - q^2) \) and different crosslink concentrations. Increasing \( \chi_m \) shifts the curve downwards. Apparently, an instability towards demixing first occurs for a nonzero wave-number \( k_c \), which maximizes the above expression.

We consider the case of a weak gel, so \( \mu(\mu - 1) \approx 1 - k^2/3 \) as the Debye function decays much more slowly than \( w(k^2)/(\mu - 1) \). In this approximation, \( k_c \) is given by
\[
0 = \frac{\partial \lambda_2}{\partial k^2} \bigg|_{k=k_c} \approx \frac{1}{3} + w'(k_c^2/(\mu - 1)), \quad (29)
\]

which leads to \( k_c^2 \approx 1.61(\mu - 1) \) and \( (1 - q^2)\chi_{\text{crit}} - 1 \approx k_c^2/(\mu - 1) = 0.98(\mu - 1) \).

A more precise numerical analysis without these approximations yields
\[
(1 - q^2)\chi_{\text{crit}} - 1 = 0.98 \cdot (\mu - 1) + 0.70 \cdot (\mu - 1)^2 + \mathcal{O}\left((\mu - 1)^3\right) \quad (30)
\]
and
\[
k_c^2 = 1.61 \cdot (\mu - 1) + 1.75 \cdot (\mu - 1)^2 + \mathcal{O}\left((\mu - 1)^3\right). \quad (31)
\]

The instability for nonzero \( k \) implies that the gel undergoes microscopic (rather than macroscopic) phase separation. This is to be expected, because crosslinks permanently connect different chains and thus prevent true macroscopic phase separation. The “next best” state for the system is phase separation up to the length-scale of the network, i.e. the typical mesh size, as given by the average localization length \( \bar{\xi} \sim (\mu - 1) \). Hence the instability occurs at a critical wave-number \( k_c \sim 1/\bar{\xi} \).

The instability is hampered by an increased density \( \mu \) of crosslinks and the asymmetry \( q \) of the composition. The spinodals for the liquid blend and two solid gels with two different degrees of crosslinking are shown in fig. 2 as a function of \( q \). In contrast, the critical wave-number remains unchanged in agreement with the above argument – the critical wave-number is determined by the mesh size, which is unaffected by \( q \). The microphase transition is addressed in section V, where it will be shown that the average charge also influences the observed microstructure.

### D. Pseudo phase diagram

Three parameters determine the state of the system: \( \mu \) controls the number of crosslinks, \( \chi_p \) specifies the charge fluctuations at preparation and \( \chi_m \) the charge fluctuations after the gel has been prepared. Each of them can be chosen such that the system is close to a critical point: \( \mu = 1 \) corresponds to the gelation transition, \( \chi_p = 1/(1 - q^2) \) to macroscopic phase separation in the preparation ensemble and \( \chi_m = \chi_{\text{crit}} \) to microphase separation in the gel.

In fig. 2, we show a phase diagram in the \( \chi_m - \mu \) plane for the special case \( q = 0 \). The spinodals of the asymmetric case can be recovered by replacing \( \chi \) by \( (1 - q^2)\chi \). The dashed line \( \mu = 1 \) separates the gel state and the liquid state. The latter is further divided into a mixed and a macroscopically phase separated liquid at \( \chi_m = 1 \) (solid line). The dotted line \( \chi_m = \chi_{\text{crit}} \) separates the mixed gel from the microphase separated one.

---

**FIG. 1:** Stability parameter \( \lambda_2(k) \) for \( \chi_m = 1/(1 - q^2) \) as a function of \( k^2 \).

**FIG. 2:** Stability limits \( \chi_{\text{crit}}(\mu) \) as a function of the asymmetry \( q \) for the liquid (\( \mu < 1 \)) and gels with different strengths (\( \mu = 1.1 \) and \( \mu = 1.5 \)).
FIG. 3: Pseudo phase diagram of the polymer blend in the $\chi$-$\mu$-plane. The state of the system is, however, history-dependent (see text for details).

The diagram in fig. 3 is not a true equilibrium phase diagram, because the state of the system also depends on the preparation ensemble through $\chi_p$. In particular, the microphases are only obtained if crosslinking takes place in the homogeneously mixed phase. As a consequence, the transition line $\mu = 1$ cannot be crossed from the macro- to the microphase separated state for $\chi_m > 1$. The history of the gel is indicated by a path in the diagram. Of particular interest are the three paths $\alpha$, $\beta$, and $\gamma$. Path $\alpha$ amounts to crosslinking close to macroscopic phase separation, $\chi_p \to 1$, and the endpoint $A$ corresponds to a homogeneously mixed gel having long-ranged frozen-in charge fluctuations. Along path $\beta$ the system is crosslinked in a preparation state that is far away from macroscopic phase separation. The endpoint $B$ corresponds to a homogeneously mixed and rather weak gel, just crosslinked enough to be solid-like. Along path $\gamma$, the system is prepared in the same way as on path $\beta$, however more crosslinks are introduced, which strengthens the gel. Subsequently, the temperature is lowered (the incompatibility $\chi_m$ increased), so that the endpoint $C$ is close to microphase separation. These three histories are representative in the following sense. Each endpoint corresponds to a state close to one critical point, as discussed above: point $A$ is close to macroscopic phase separation in the preparation ensemble, $\chi_p = 1$; point $B$ is close to the gelation transition, $\mu = 1$; and point $C$ is close to microphase separation, $\chi_m = \chi_{\text{crit}}$. The three states of the system, corresponding to the endpoints, will be discussed in detail in the following sections.

E. Charge density correlations in the mixed gel

In this section we discuss the homogeneously mixed gel phase, for which the order parameter for phase separation vanishes. Nevertheless, there are thermal as well as quenched charge fluctuations on various length-scales. These can be detected with help of multiple correlation functions. On the Gaussian level of approximation, these correlation functions are given by the inverse of the Hessian matrix (24):

$$\langle \Psi_{k}^{\alpha_1} \Psi_{k}^{\alpha_2} \rangle_{n+1} = (A^{-1})_{\alpha_1 \alpha_2}. \quad (32)$$

The correlator that is off-diagonal in replica space accounts for the frozen-in correlations and will be termed the glassy correlator. It is given by

$$S_{gl}(k) := \langle [\tilde{\Psi}_{-k}] [\tilde{\Psi}_{k}] \rangle = \lim_{n \to 0} \langle \Psi_{k}^{n} \Psi_{-k}^{n} \rangle = \frac{1}{\chi_{m}} \cdot \frac{b(b+c)}{c\lambda_2^2}; \quad (33)$$

see eq. 8 for the definition of $\tilde{\Psi}$. The replica-diagonal correlator is the scattering intensity

$$S_{sc}(k) := \langle \tilde{\Psi}_{-k} \tilde{\Psi}_{k} \rangle = \lim_{n \to 0} \langle \Psi_{k}^{n} \Psi_{-k}^{n} \rangle = \frac{1}{\chi_{m}} \cdot \left( \frac{b(b+c)}{c\lambda_2^2} + \frac{1}{\lambda_2} - \chi_{m} \right), \quad (34)$$

and the variance (or connected correlator) is given by

$$S_{var}(k) := S_{sc}(k) - S_{gl}(k) = \frac{1}{\chi_{m}} \cdot \left( \frac{1}{\lambda_2} - \chi_{m} \right). \quad (35)$$

Whereas the glassy correlator $S_{gl}(k)$ describes the static, frozen-in correlations, the variance $S_{var}(k)$ quantifies the volatile, thermal fluctuations about the mean value. The scattering intensity $S_{sc}(k)$ is the sum of both contributions and covers both, thermal and static charge inhomogeneities.

Restriction to symmetric blends

In the following discussion of $S_{sc}(k)$, $S_{gl}(k)$ and $S_{var}(k)$ we shall confine ourselves to the case of symmetric blends, yet without loss of generality: The scattering functions of the asymmetric case are recovered via multiplication by $\gamma = (1 - q^2)$ and the rescalings $\chi_p \to \gamma \chi_p$ and $\chi_m \to \gamma \chi_m$. Furthermore, the distance to phase separation is replaced with the distance to the spinodal in the asymmetric case. In the range between the equilibrium phase transition and the spinodal, the results then describe an undercooled mixture.

Length-scales

The correlation functions are characterized by three length-scales which are determined by the parameters $(\mu, \chi_p, \chi_m)$ of preparation and measurement conditions:

First, there is the typical localization length $\xi$ of the monomers in the gel fraction, i.e. the mean mesh size of the gel. From eq. (22) we can infer that this length-scale is roughly given by

$$\xi_{l} := 1 / \sqrt{\mu - 1}. \quad (36)$$
Second, there is the decay length $\xi_p$ of the pre-critical demixing fluctuations prior to gelation. This approximately reads

$$\xi_p := 1/\sqrt{1 - \chi_p}. \quad (37)$$

The third length characterizes the pre-critical fluctuations of microphase separation, and is approximately given by

$$\xi_m := 1/\sqrt{\chi_{cr} - \chi_m}. \quad (38)$$

The three length-scales measure, or are given by, the inverse distance to the phase transitions of gelation and demixing in the pre-crosslinking blend, and microphase separation in the gel; hence they grow large when approaching their respective transitions. In the following, we shall essentially discuss three limiting regimes, in which the correlation functions are determined by one of the three length-scales

- $\xi_p \gg \xi_l, \xi_m$ (point A),
- $\xi_l \gg \xi_p, \xi_m$ (point B), and
- $\xi_m \gg \xi_l, \xi_p$ (point C).

**Glassy correlations**

The glassy correlation function $S_{gl}(k)$ describes *time-persistent* charge inhomogeneities due to crosslinking. If the preparation ensemble is close to phase separation then instantaneous crosslinking will freeze in these fluctuations, and $S_{gl}$ will be dominated by the pre-crosslinking fluctuations, giving rise to a high value at zero wavevector. If, on the other hand, the preparation ensemble is in a well-mixed state then crosslinking will introduce *completely random, static* charge fluctuations, which subsequently can be enhanced by approaching the microphase separation transition in the gel. In the following, we discuss the three limiting cases (i.e. points A, B, C) in detail.

We first consider a gel that is prepared from a melt close to phase separation, i.e. $\xi_p \gg (\xi_l, \xi_m) \gg 1$, corresponding to point A in fig. 3. The network can freeze-in correlations on length-scales larger than or comparable to its mesh size. For $\xi_p \gg \xi_l$, the pre-crosslinking fluctuations have long enough scales to be frozen. Consequently, the glassy correlations reflect the pre-crosslinking fluctuations:

$$S_{gl}(k) \propto \frac{\xi_p^2}{1 + k^2 \xi_p^2/3}. \quad (39)$$

The glassy correlations are proportional to $\xi_p^2$ and decay on the scale $k \sim \xi_p^{-1}$ set by the fluctuations of the *preparation ensemble*. An example is included in fig. 4.

In a weak gel, i.e. if $\xi_l \gg (\xi_p, \xi_m) \gg 1$ (point B), the network is rather wide-meshed, so that the fluctuations at preparation cannot be frozen in. Instead, there will be static charge fluctuations $\langle \tilde{\Psi}_k \rangle \neq 0$ on the scale of the network, which are completely random and hence vanish, if averaged over crosslink configurations, $\langle \tilde{\Psi}_k \rangle = 0$. They do, however, contribute to the glassy correlations, which are given approximately by

$$S_{gl}(k) \approx \frac{1}{2} Q \xi_m^4 \cdot w(k^2 \xi_l^2). \quad (40)$$

These fluctuations always decay on the length-scale of localization, but they are enhanced in magnitude when approaching microphase separation. An example of the glassy correlations in this range is given in fig. 5.

The cross-over between the two scales is demonstrated in fig. 6, which shows $S_{gl}(k)/S_{gl}(0)$ far from microphase separation for $\xi_l = 10$. For the leftmost curve $\xi_p^2 = 10^5 \gg \xi_l^2 = 100$, and hence the decay occurs at $k \sim \xi_p^{-1}$. Upon decreasing $\xi_p$, the curves shift to the right, until, for $\xi_l \gg \xi_p$, the decay is determined by $\xi_l$. The inset shows the
the peak diverges as \( k \to 0 \). An example is included in fig. 7. Approaching the transition, \( \xi_{C} \) develops a peak at \( k_{C} \), towards macroscopic demixing. In the gel, displacements of crosslinks there would be large-scale fluctuations towards microphase separation. In the absence of crosslinks there would be large-scale fluctuations towards macroscopic demixing. In the gel, displacements are bounded by the localization length, so that \( S_{gl}(k) \) develops a peak at \( k_{C} \sim \xi_{C}^{-1} \), where \( \lambda_{2}(k) \) becomes small; an example is included in fig. 7. Approaching the transition, the peak diverges as \( \lambda_{2}^{-2}(k) \), and the glassy correlations can be approximated by

\[
S_{gl}(k) \propto \frac{Q}{\xi_{m}} \left( \chi_{\text{crit}}(\mu) - \chi_{m} + \frac{1}{2}(k^{2} - k_{C}^{2})^{2}w''(1) / k_{C}^{2} \right),
\]

where \( w'' \) denotes the second derivative of the scaling function introduced below eq. (22) and defined in appendix C.

**Thermal fluctuations**

The variance \( S_{\text{var}}(k) \) of the charge fluctuations is independent of the conditions at the time of crosslinking. Hence, there are only two competing length-scales, \( \xi_{l} \) and \( \xi_{m} \). In case of a weak gel, i.e. \( \xi_{l} \gg \xi_{m} \gg 1 \) (point B in fig. 3), eq. (35) reduces to

\[
S_{\text{var}}(k) \approx \frac{\xi_{m}^{2}}{1 + k^{2} \xi_{m}^{2}/3}.
\]

for small \( k \), decaying with a half-width of \( k_{1/2} \approx \sqrt{3}/\xi_{m}^{2} \), provided \( \xi_{m} \) is not too small. Far away from the demixing threshold, the fluctuations are hardly affected by the network and look like critical fluctuations approaching macroscopic phase separation. An example is shown in fig. 5.

Close to microphase separation, i.e. \( \xi_{m} \gg \xi_{l} \gg 1 \) (point C), the fluctuations grow with increasing \( k \) until \( k \) reaches the inverse localization length \( k \sim \xi_{l}^{-1} \), beyond which they are strongly suppressed by the network. The variance is approximately given by

\[
S_{\text{var}}(k) \approx \frac{1}{\lambda_{2}(k)} \frac{1}{\chi_{\text{crit}}(\mu) - \chi_{m} + \frac{1}{2}(k^{2} - k_{C}^{2})^{2}w''(1) / k_{C}^{2}},
\]

revealing a peak at \( k_{0} \approx 1/\xi_{l} \) that has a height proportional to \( \xi_{m}^{2} \). See fig. 3 for an example.

**Scattering intensity**

The behavior of the scattering function in the various regimes can be inferred from the behaviors of \( S_{gl}(k) \) and \( S_{\text{var}}(k) \), as \( S_{sc}(k) \) is just the sum of them. A weak gel (point B) preserves only a small amount of the pre-crosslinking fluctuations and can hardly restrict thermal fluctuations. Hence, \( S_{sc}(k) \approx S_{\text{var}}(k) \), so the scattering function decays on the scale \( k \sim \xi_{C} \); see fig. 4. In the other regimes, thermal fluctuations are suppressed by the network, and \( S_{sc}(k) \approx S_{gl}(k) \). In a gel prepared close to phase separation (point A), the scattering function decays on the scale \( k \sim \xi_{p} \) (fig. 2), whereas a gel measured close to microphase separation (path C) reveals a peak at \( k \sim k_{0} \), diverging at the transition (fig. 5).
V. MICROSTRUCTURES

At $\chi_m = \chi_{\text{crit}}$, the homogeneous gel becomes unstable with respect to phase separation. As we have seen in section [11], the instability first occurs for nonzero wave-numbers, indicating that the gel undergoes microscopic rather than macroscopic phase separation. In this section we investigate various microstructures, such as hexagons and lamellae with a definite orientation, as well as a superposition of many random orientations. The selection of a particular microstructure depends sensitively on the compressibility and the charge imbalance. We first discuss the simplest case of incompressible, symmetric mixtures, and then go on to investigate the effects of charge imbalance and compressibility.

Incompressible, symmetric mixtures

Our analysis of microphase separation is based on the effective free energy [12] in the gel phase. We expand it around $\Psi = 0$ up to fourth order, in the presence of a nonzero gel order parameter $\Omega$ given by eq. (22). The expansion reads

$$\frac{1}{2} \sum_{\alpha} \sum_k A_{\alpha_1 \alpha_2}(k) \Psi_{\alpha_1}^k \Psi_{\alpha_2}^k$$

$$+ \frac{1}{2} \sum_{\alpha} \sum_{k_1, k_2} \sum_{k_3} \psi \left( \frac{g_3(k_1, k_2) g_3(k_3, k_4)}{g_0((k_1 + k_2)^2)} - \frac{g_{\psi}(k_1, k_2, k_4)}{3} \right) \Psi_{\alpha_1}^k \Psi_{\alpha_2}^k \Psi_{\alpha_3}^k \Psi_{\alpha_4}^k \tag{44}$$

Here, $A_{\alpha_1 \alpha_2}(k)$ is given in eqs. (24,27), and the vertex of the fourth-order term is given by the Wiener correlators

$$g_3(k_1, k_2) = \int_0^1 ds_1 ds_2 ds_3 \left< e^{-i \sum_{\nu=1}^3 k_\nu r(s_\nu)} \right|_{k_3 = -k_1 - k_2}$$

and

$$g_{\psi}(k_1, k_2, k_3) = \int_0^1 ds_1 ds_2 ds_3 ds_4 \left< e^{-i \sum_{\nu=1}^4 k_\nu r(s_\nu)} \right|_{k_4 = -\sum_{\nu=1}^3 k_\nu} \tag{45}$$

(see appendix [3]).

At the onset of the microphases, the amplitude goes to zero continuously, and the optimal wave-number is given by $k_c$ [see eq. (21)], implying a domain-size of the order of the localization length of the gel. Beyond the critical point, the amplitude is nonzero, and the wavenumber deviates from its critical value $k_c$. Both are obtained from a variational optimization of the above free energy:

$$\psi^2_{\text{min}}(k) = -\frac{\lambda_2(k)}{g_4(k^2)} \tag{50}$$

and

$$k_{\text{min}}^2 - k_c^2 = c_0 \cdot (\chi_m - \chi_{\text{crit}}) + O((\chi_m - \chi_{\text{crit}})^2) \tag{51}$$

The constant $c_0$ can be computed analytically only for a weak gel, by further expansion in powers of $\mu - 1$,
which yields \( c_0 \approx 2.03 (\mu - 1) \). The optimal amplitude \( \psi_{\min}(k_{\min}) \) grows continuously with \( \chi_m - \chi_{\text{crit}} \):

\[
\psi_{\min}^2 = \frac{\chi_m - \chi_{\text{crit}}}{\chi_{\text{crit}} g_4(k_c^2)} + \mathcal{O}((\chi_m - \chi_{\text{crit}})^2). \quad (52)
\]

Other simple structures, such as a hexagonal stack of cylinders or a bcc crystal of spheres, have higher free energies. The same holds for a superposition of several sinusoidal modulations like eq. (47), with the same wave-numbers but different directions. As we shall see below, these conclusions depend on the symmetry of the mixture and its incompressibility.

**Effects of asymmetry**

The most important effect of the asymmetry is a third-order term in the Landau expansion, rendering both the macrophase separation of the uncrosslinked liquid and the microphase separation of the gel first-order transitions.

To keep the discussion simple, we neglect deviations of \( k^2 \) from \( k_c^2 \) and drop the \( k \)-dependence of the higher-order terms in the Landau free energy. With the ansatz \( \Psi_k^m = (1 - \delta_{m,0}) \psi_k \), corresponding to the mixed state in the preparation ensemble and replica-symmetric phase separation in the measurement ensemble, this leads to the free energy density

\[
f \left( \{ \Psi \} \right) = \frac{1}{1 - q^2} \left[ \sum_k \lambda_2(k) \psi_k \psi_{-k} + \frac{q}{3} \sum_{k_1,2,3} \psi_{k_1} \psi_{k_2} \psi_{k_3} \cdot \delta_{k_1+k_2+k_3,0} \right.
\]

\[
+ \frac{q^2}{2} \left( \sum_k \psi_k \psi_{-k} \right)^2 + \frac{1 - 3q^2}{12} \sum_{k_1,2,3,4} \psi_{k_1} \psi_{k_2} \psi_{k_3} \psi_{k_4} \cdot \delta_{k_1+k_2+k_3+k_4,0} \right]. \quad (53)
\]

with \( \lambda_2(k) \) defined in eq. (27).

Besides the lamellar microphases already discussed in section [\ref{microphases}], we now consider two additional morphologies: Cylindrical phases having parallel orientation, aligned on a honeycomb lattice in the perpendicular plane, and spherical domains on a body centered cubic lattice. Although a randomly crosslinked blend will probably reveal only local order, the regular structures are useful for constructing a simple and tractable ansatz for the microphase separated state:

\[
\Psi_p = \frac{\Psi}{\sqrt{m}} \sum_{i=1}^m (\delta_{p, kn_i} + \delta_{p, -kn_i}) \quad (54)
\]

with \( m = 1 \) for lamellae, \( m = 3 \) for hexagonally ordered cylinders, and \( m = 6 \) for spheres on a bcc lattice, and the corresponding lattice vectors \( \{ n_i \} \) being defined in appendix [\ref{Appendix A}].

With the lattice ansatz (54), the evaluation of the higher-order sums in eq. (53) amounts to counting the number of possible “loops” of two, three and four lattice vectors that add to zero. This is carried out in appendix [\ref{Appendix A}], yielding \( \sum_k \psi_k \psi_{-k} = 2 \Psi^2 \), independent of the morphology, and also

\[
\sum'_{k_1,2,3} \psi_{k_1} \psi_{k_2} \psi_{k_3} \cdot \delta_{k_1+k_2+k_3,0} = c_3^{(m)} \Psi^3, \quad (55)
\]

\[
\sum'_{k_1,2,3,4} \psi_{k_1} \psi_{k_2} \psi_{k_3} \psi_{k_4} \cdot \delta_{k_1+k_2+k_3+k_4,0} = c_4^{(m)} \Psi^4, \quad (56)
\]

where

\[
c_3^{(1)} = 0, \quad c_3^{(3)} = 4/\sqrt{3}, \quad c_3^{(6)} = 4 \cdot \sqrt{2}/3, \quad (57)
\]

\[
c_4^{(1)} = 6, \quad c_4^{(3)} = 10, \quad c_4^{(6)} = 15. \quad (58)
\]

Thus, the free-energy density becomes

\[
f \left( \{ \Psi \} \right) = \frac{\chi_m - \chi_{\text{crit}}}{1 - q^2} \Psi^2 + \frac{q^3 c_3^{(m)}}{3} \Psi^3 + \frac{2q^2 + (1 - 3q^2)c_4^{(m)}}{12} \Psi^4. \quad (59)
\]

Here, \( \lambda_2 \) has been evaluated at \( k_c \) because (in this section) we are not considering deviations of the wave-number from its critical value.

For \( m = 1 \), the third-order term vanishes, even if \( q \neq 0 \), so the transition remains second order and the spinodal indeed indicates the equilibrium phase transition point
with respect to lamellae. In contrast, for cylinders and bcc spheres the equilibrium transition point $\chi_t$ is shifted according to

$$\frac{1}{(1-q^2)\chi_t} - \frac{1}{(1-q^2)\chi_{\text{crit}}} = \frac{(q_{c1}^{(m)}/3)^2}{4(2q^2 + (1-3q^2)c_4^{(m)}/12)}$$

$$= \frac{(q_3^{(m)})^2}{72q^2 + 3(1-3q^2)c_4^{(m)}}$$

$$= \left\{ \begin{array}{ll}
4q^2/45 - 27q^4 & \text{for } m = 3 \\
32q^2/135 - 189q^2 & \text{for } m = 6
\end{array} \right. (\text{bcc spheres})$$

(60)

In the asymmetric case, the bcc spheres yield the lowest equilibrium transition point of the three possibilities considered, i.e. microphases first occur with bcc symmetry. This is to be expected, as the ratio of surface to volume of the minority phases is minimal for spheres embedded in the majority phase, and is in agreement with the finding of Alexander and McTague [13] of a general preference for bcc symmetry in crystal nucleation. Note, however, that the Landau expansion is only valid for small absolute charge density, and condensing regions contacts and lower its energy by diluting mixed regions having a single wave-vector $k$ as in eq. (47), eq. (61) predicts density-field modulations having wave-vector $k_1 = \pm 2k$, i.e. with twice the wave-number of the charge-density modulations. This is intuitively clear: Along one spatial period of the charge-density modulations, their modulus or square, and thus the mass density, oscillates twice, corresponding to the half wave-length or the double wave-number; this is illustrated in fig. 8.

The compressibility is controlled by the strength of the excluded volume interaction, i.e. the parameter $\lambda = \lambda_m - \mu/V^n$. To study microphase separation in the asymmetric but compressible case, we integrate out the density field, keeping $\lambda$ finite. With the ansatz $\Psi^\alpha = (1-\delta_{\alpha,0})\Psi$, we obtain

$$f(\Psi) = \frac{1}{2} \sum_k' \lambda_2(k) \Psi_k \Psi_{-k} + \frac{1}{8\lambda_{\text{eff}}} \left( \sum_k \Psi_k \Psi_{-k} \right)^2$$

$$+ \frac{1}{12} \left(1 - \frac{3}{2\lambda_{\text{eff}}} \right) \sum_{k_1,2,3,4} \Psi_{k_1} \Psi_{k_2} \Psi_{k_3} \Psi_{k_4} \times \delta_{k_1+k_2+k_3+k_4,0}. \quad (62)$$

(62)

Here, $\lambda_{\text{eff}} = \lambda - \mu + 1$, and we have dropped the $k$ dependence in the higher-order vertices, thereby restricting the domain size to its critical value, determined by $k_c$ or the localization length of the gel.

To account for the potential randomness of the microphase pattern, we extend the previous lamellar ansatz by allowing a superposition of $Z$ one-dimensional waves, each with identical wave-number $k_c$ but random phases $\Phi_z$ and wave-vector orientations $n_z$, i.e.,

$$\Psi_k = \Psi \sqrt{Z} \sum_{z=1}^Z (e^{i\Phi_z} \delta_{k-k_c,n_z} + e^{-i\Phi_z} \delta_{k+k_c,n_z}), \quad (63)$$

corresponding to $2\Psi/(\sqrt{Z}Z^{1/2}) \cdot \sum_{z=1}^Z \cos(k_c n_z x + \Phi_z)$ in real space. The optimal number of orientations will be determined later. A few examples of such random morphologies are shown in fig. 8; the number of phases ranging from 1 to 100.

We assume that none of the orientations $n_z$ are collinear, and thus the quadratic sums in eq. (62) yield

$$\sum_k' \lambda_2(k_c) \Psi_k \Psi_{-k} = 2\lambda_2(k_c) \Psi^2$$

(64)

$$\sum_k' \Psi_k \Psi_{-k} = 2\Psi^2. \quad (65)$$

Effects of compressibility

A compressible system can avoid unfavorable $A$-$B$ contacts and lower its energy by diluting mixed regions having many such contacts, which are characterized by a small absolute charge density, and condensing regions that are rich in either $A$ or $B$, which have a high absolute charge density. Mathematically, this becomes apparent via a nonzero value of the saddle-point of the density $\rho$ in a phase separated state. For simplicity, we restrict the discussion of compressibility effects to the symmetric case, where the shifted and the original density fields coincide. In this case, the saddle point of $\rho$ is given by

$$\rho_k^\alpha = \frac{i}{2(1/\lambda^\alpha + g_d(k^2))} \sum_{k_{1,2}}' \Psi_{k_1}^\alpha \Psi_{k_2}^\alpha \cdot \delta_{k+k_1+k_2,0}. \quad (61)$$

For the simple example of lamellar microphases described by a single wave-vector $k$ as in eq. (47), eq. (61) predicts density-field modulations having wave-vector $k_1 = \pm 2k$, i.e. with twice the wave-number of the charge-density modulations. This is intuitively clear: Along one spatial period of the charge-density modulations, their modulus or square, and thus the mass density, oscillates twice,
To compute the fourth-order sum in eq. (62), we have to count the number of possible closed loops of orientations. Because of the randomness, the existence of quadruples of orientations able to form a closed loop is very unlikely, except for the degenerate planar case of pairs of opposite vectors \((\pm n_z, \pm n_{z'})\), and hence we disregard non-planar loops. Single orientations allow for the construction of quadruples \((n_z, n_z, -n_z, -n_z)\) that can be ordered in \(\binom{4}{1} = 6\) ways. Quadruples \((\pm n_z, \pm n_{z'})\) of two pairs of different orientations can be ordered in \(4! = 24\) different ways, and there are \(\frac{5}{2}Z(Z - 1)\) such pairs. Thus, the quartic sum in eq. (62) yields

\[
\sum_{k_{1,2,3,4}}' \Psi_{k_1} \Psi_{k_2} \Psi_{k_3} \Psi_{k_4} \delta_{k_1+k_2+k_3+k_4,0} = \frac{12Z(Z - 1) + 6Z}{Z^2} \Psi^4 = 12\left(1 - \frac{1}{2Z}\right) \Psi^4. \quad (66)
\]

Inserting the sums into the free-energy density we obtain

\[
f(\Psi) = \lambda_2(k) \Psi^2 + \left(1 - \frac{1}{\lambda_{eff}}\right) - \left(1 - \frac{3}{2\lambda_{eff}}\right) \frac{1}{2Z} \Psi^4. \quad (67)
\]

The fourth-order term depends on \(\lambda_{eff}\) and the number of components \(Z\). It has to be positive to guarantee stability, and this requires \(\lambda_{eff} > 1\). The sign of the \(O(Z^{-1})\) term determines the optimal number of random orientations. For low compressibilities, \(i.e.\) for \(\lambda_{eff} > 3/2\), the term is negative and the free energy grows with an increasing number of orientations, hence the simple lamellar morphology is favored. For a rather compressible system having, in contrast, \(1 < \lambda_{eff} < 3/2\), the effective free energy decreases with increasing \(Z\), favoring an “infinite” number of orientations and hence a random pattern.

\section{VI. CONCLUSIONS}

In this paper we have analyzed a microscopic model of crosslinked polymer blends, built on the Edwards model for a polymer melt and generalized to two components, which are mutually incompatible. Random crosslinks are introduced according to the Deam-Edwards distribution, also generalized to include concentration fluctuations at the instant of crosslinking. Thereby, the concentration fluctuations in the melt are partially frozen in and sustained in the gel phase. Apart from these correlations, which are present at preparation, the crosslinks are taken to connect monomers irrespective of their charge. Hence, within mean-field theory, the resulting gel is identical to the one made from just one species of polymer. However, concentration fluctuations are present, and have been computed on the Gaussian level of approximation. Of particular interest are the frozen-in or glassy fluctuations, which reflect the preparation state. In general, the network can only quench fluctuations on length-scales larger than its own mesh size, which is roughly given by the localization length of mean-field theory. If the preparation ensemble is close to macroscopic phase separation then the length-scale of these fluctuations is large compared to the mesh size, so that the glassy fluctuations are given by the concentration fluctuations in the preparation state. If, on the other hand, the preparation state is far from phase separation, the frozen-in charge fluctuations follow the network pattern, and hence are completely random, because the crosslinks are not sensitive to the species. The thermal concentration fluctuations are independent of the preparation state.

Lowering the temperature in the gel, or equivalently increasing the incompatibility of the two species, gives rise to phase separation, the spatial extent of which is limited by the mesh size of the network. The length-scale of the resulting “micro”-phases can thus range from almost microscopic to nearly macroscopic scales, depending on the degree of crosslinking of the gel. The instability towards microphase separation is signaled by a divergence of the time-persistent as well as the thermal fluctuations. The emergent microstructure is shown to depend sensitively on charge imbalance and compressibility. The latter allows for random patterns with a unique wave-length, \(i.e.,\) the localization length, whereas in the incompressible system lamellae are favorable for balanced mixtures and hexagonal patterns for imbalanced mixtures.

We now compare our results to previous phenomenological approaches, many of which have focused on the issue of microphase separation. de Gennes argued that the charges in the crosslinked gel cannot move freely but are displaced in analogy to the charges in a dielectric material. He introduced a polarization \(P\) which, as in electrostatics, is determined by the charges according to \(\nabla \cdot P = -\Psi\). In the limit of weak segregation, the free energy is quadratic in the polarization, and is simply added to the free energy of charge fluctuations, resulting in

\[
f(\{\Psi\}) = \frac{1}{2} \sum_k (\chi_{crit} - \chi_m + k^2 + \frac{C}{k^2}) \Psi_k \Psi_{-k},
\]

where \(C\) is a coefficient of “internal rigidity”. The above free energy leads to an instability at finite wave-number (microphase separation), but predicts that \(\lim_{k \to 0} S_c(k) = 0\), in disagreement with experiment.
The nonzero scattering intensity at zero wave-number is due to the frozen-in charge fluctuations present at preparation. To account for these fluctuations, Benhamou et al. \cite{Benhamou98} refined the analogy to a dielectric by including a Debye-Hückel screening of the “charges”, which permits long-range inhomogeneities leading to a non-vanishing zero-angle scattering. The screening length \( \kappa \) is determined self-consistently, by assuming that the scattering intensity at \( k = 0 \) is not affected by the crosslinking as long as the temperature remains unchanged after preparation \cite{Bird94}. The free energy in the quadratic approximation then reads:

\[
\begin{align*}
  f (\{\Psi\}) &= \frac{1}{2} \sum_k' \left( \frac{1}{\chi_m} - g_D(k^2) + \mu(\mu - 1)\omega(k^2(\mu - 1)) \right) \Psi_k \Psi_{-k} \\
  &\approx \frac{1}{2} \sum_k' \left( 1 - \chi_m + k^2\frac{\chi_m}{3} + \mu(\mu - 1)\omega(k^2(\mu - 1)) \right) \Psi_k \Psi_{-k}.
\end{align*}
\]  

(69)

(70)

(71)

In the last line, we have expanded the Debye function for small wave-number. We see that the microscopic model indeed agrees with phenomenological theories, provided we identify the phenomenological terms with the order parameter of the gel. The wave-number dependence of the order parameter is not a Lorentzian; nevertheless, it decays monotonically with \( k \), the relevant length-scale being given by the localization length. Hence, the somewhat mysterious screening length is unambiguously identified with the localization length, which is computed self-consistently. Thereby, the microscopic model substantiates the picture of de Gennes and, furthermore, allows the computation of the parameters and functions that are beyond the phenomenological approach.

The frozen-in fluctuations were first addressed by Read et al. \cite{Read92}, who considered a blend of polymer chains anchored at both ends to randomly chosen fixed points in space, in order to account approximately for the localization of chains due to the crosslinks. Read et al. make reasonable but ad hoc assumptions about the distribution of the quenched random end-to-end vectors, and solve the resulting model within the random phase approximation. They obtain a scattering function that exhibits a nonzero value at \( k = 0 \) is not affected by the crosslinking as long as the temperature remains unchanged after preparation \cite{Bird94}. The free energy in the quadratic approximation then reads:

\[
\begin{align*}
  f (\{\Psi\}) &= \frac{1}{2} \sum_k' \left( \frac{1}{\chi_m} - g_D(k^2) + \mu(\mu - 1)\omega(k^2(\mu - 1)) \right) \Psi_k \Psi_{-k} \\
  &\approx \frac{1}{2} \sum_k' \left( 1 - \chi_m + k^2\frac{\chi_m}{3} + \mu(\mu - 1)\omega(k^2(\mu - 1)) \right) \Psi_k \Psi_{-k}.
\end{align*}
\]

(69)

(70)

(71)

Both approaches, the phenomenological one and the microscopic model, predict a divergence as microphase separation is approached, with the glassy correlations diverging twice as strongly as the thermal ones.

The work reported in the present paper can be extended in several directions. First, we have worked only on the level of mean-field and Gaussian fluctuations. It is known that the microphase separation transition in the symmetric case is rendered first order by fluctuations \cite{Kob93}, and hence it would be interesting to see the effect of fluctuations, even though the critical region is expected to be small \cite{Kob97}. Another extension is a crosslink probability that depends on the species. This would allow us to study, among other things, interpenetrating networks. Finally, it would be interesting to look at the dynamics of microphase separation.

**APPENDIX A: MICROPHASE MORPHOLOGY**

To investigate microphase transition, we assume that the phase-separation pattern can be described by a first-harmonic ansatz having a dominant wave-number \( k \) and a definite lattice structure:

\[
\Psi_k = \Psi \frac{V}{\sqrt{2m}} \sum_{i=1}^{m} \delta_{k';+k_n_i} + \delta_{k';-k_n_i},
\]

(A1)

with lattice vectors \( n_i \in G := \{n_i | i = 1 \ldots m\} \) and an amplitude \( \Psi \).
1. Lattice structures

We consider three particular morphologies, which are known to occur in the microphase separation of regular copolymer melts [17, 18]:

**lamellae** \((m = 1)\): Alternating sheets rich in \(A\) and \(B\); one-dimensional order. Lattice vector: \(n_1 = (1, 0, 0)^T\).

**cylinders** \((m = 3)\): Close-packed, i.e. hexagonally arranged, cylindrical domains, \(A\) in \(B\) or vice versa; two-dimensional order. Lattice vectors: \(n_1 = (1, 0, 0)^T\), \(n_2 = (-1/2, \sqrt{3}/2, 0)^T\) and \(n_3 = (-1/2, -\sqrt{3}/2, 0)^T\).

**bcc spheres** \((m = 6)\): Spherical \(A\)-rich domains in \(B\), or vice versa, on a bcc lattice in real space; three-dimensional order. Lattice vectors of the corresponding fcc lattice in Fourier space:

\[
\sum_{k_1, \ldots, p}^\prime f_2(k_1, \ldots, k_{p-1}) \Psi_{k_1} \cdots \Psi_{k_p} \delta_{\sum_{i=1}^p k_i, 0}
= \frac{\Psi^p \cdot V^p}{(2m)^{p/2}} \sum_{k_1, \ldots, p}^\prime f_2(k_1, \ldots, k_{p-1}) \prod_{\nu=1}^p \left( \sum_{\mu=1}^m (\delta_{k_{\nu}, k_{\mu}} + \delta_{k_{\nu}, -k_{\mu}}) \right) \delta_{\sum_{\nu=1}^p k_{\nu}, 0}
= \Psi^p \cdot \frac{V^p}{(2m)^{p/2}} \sum_{k_1, \ldots, p \in \mathbb{G}^+} f_2(k_1, \ldots, k_{p-1}) \delta_{k_1 + \cdots + k_p, 0} \quad (A2)
\]

In the quadratic sum the vertex function can be factored out, so that

\[
\frac{1}{V^2} \sum_{k'} f(k^2) \Psi_{k'} \Psi_{-k'}
= \Psi^2 \cdot \frac{f(k^2)}{2m} \sum_{k_{1,2} \in \mathbb{G}^+} \delta_{k_{1,2}, 0} = \Psi^2 \cdot f(k^2) \quad (A3)
\]

The higher-order sums, however, strongly depend on the morphology of the microphases. In the simplest case, \(f(k_1, \ldots) = 1\), the computation of these loops amounts to counting the number of closed loops that can be constructed with the vectors in \(\mathbb{G}^+\). In general, the loops must also be classified with respect to their shape, i.e. planar or non-planar, as distinct shapes yield distinct values of the vertex functions. The counting and classification have been done, e.g., in [18], with the results shown in Table I. For \(f(k, \ldots) = 1\), the third- and fourth-order sums are given by

\[
\frac{1}{V^3} \sum_{k_1, 2} \Psi_{k_1, k_2} \Psi_{-k_1 - k_2}
= \Psi^3 \cdot \begin{cases} 0 & \text{for } m = 1 \text{ (lamellae)}, \\ \sqrt{2/3} & \text{for } m = 3 \text{ (cylinders)}, \\ 2/\sqrt{3} & \text{for } m = 6 \text{ (bcc spheres)}, \end{cases} \quad (A4)
\]

| loop type | lamellae | cylinders | bcc spheres |
|-----------|---------|-----------|-------------|
| 2-loop    | 2       | 6         | 12          |
| 3-loop    | 0       | 12        | 48          |
| 4-loop planar | 6   | 90        | 396         |
| nonplanar | -       | -         | 144         |
| total     | 6       | 90        | 540         |

TABLE I: Number of closed loops of \(p\) lattice vectors ("\(p\)-loops") for different morphologies. The 4-loops are divided into intra- and extra-planar loops.
and

\[ \frac{1}{\sqrt{\gamma}} \sum_{k_{1,2,3}} \Psi_{k_1} \Psi_{k_2} \Psi_{k_3} \Psi_{-k_1-k_2-k_3} \]

\[ = \Psi^4. \begin{cases} 3/2 & \text{for } m = 1 \text{ (lamellæ)}, \\ 5/2 & \text{for } m = 3 \text{ (cylinders)}, \\ 15/4 & \text{for } m = 6 \text{ (bcc spheres)}. \end{cases} \]

**APPENDIX B: VERTEX FUNCTIONS**

In the following, we define and compute the vertex functions appearing in the Landau expansion of the effective free energy, which are integrals over Wiener correlators of the type

\[ \left\langle \exp \left\{ -i \sum_{\zeta,\zeta'} \hat{k}_\zeta \cdot \hat{r}(s_{\zeta}) \right\} \right\rangle_W \]

\[ = \delta_{\sum_{\zeta=1}^{z_1} k_{\zeta}, 0} \exp \left\{ \frac{1}{2} \sum_{\zeta,\zeta'} |s_{\zeta} - s_{\zeta'}| \hat{k}_\zeta \cdot \hat{k}_{\zeta'} \right\}; \]

\[ (B1) \]

a derivation of eq. \[(B1)\] can be found in \[(B2)\]. The correlator vanishes unless the wave-vectors sum to zero in each replica. If just single-replica quantities are involved, the correlator factorizes,

\[ \left\langle \exp \left\{ -i \sum_{\zeta_1=1}^{z_1} k_{\zeta_1} \cdot \hat{r}(s_{\zeta_1}) \right\} \right\rangle_W \]

\[ = \left\langle \exp \left\{ -i \sum_{\zeta_1=1}^{z_1} k_{\zeta_1} \hat{r}(s_{\zeta_1}) \right\} \right\rangle_W \times \cdots \]

\[ \times \left\langle \exp \left\{ -i \sum_{\zeta_m=1}^{z_m} k_{\zeta_m} \hat{r}(s_{\zeta_m}) \right\} \right\rangle_W \]

for pairwise distinct \(\alpha_1, \ldots, \alpha_m\), where \(\langle \cdots \rangle_W\) denotes the unreplicated Wiener average.

**1. Definition of the vertex functions**

The second-order coefficients of the Landau expansion are governed by the Debye function

\[ g_2(k^2) := \int_0^1 ds_1 ds_2 \left\langle e^{-ik_1 s_1 + i k_2 s_2} \right\rangle_W \]

\[ = \int_0^1 ds_1 ds_2 \left\langle e^{-ik_1 s_1 + i k_2 s_2} \right\rangle_W \]

\[ = \frac{e^{-k_1^2 - k_2^2}}{k^2/2} = 1 - \frac{1}{4} k^2 + \frac{1}{12} k^4 + O(k^6), \]

the scattering function for a non-interacting Gaussian chain.

The third-order correlators,

\[ g_3(k_1, k_2) \]

\[ := \int_0^1 ds_1 ds_2 ds_3 \left\langle e^{-i \sum_{\nu=1}^3 k_{\nu} r(s_{\nu})} \right\rangle_W \]

\[ = \int_0^1 ds_1 ds_2 ds_3 \left\langle e^{-i \sum_{\nu=1}^3 \hat{k}_{\nu} r(s_{\nu})} \right\rangle_W \]

\[ \left| k_3 = -k_1 - k_2 \right| \]

and

\[ g_{\Psi^2 \Omega}(k_1, k_2) := \int_0^1 ds_1 ds_2 ds_3 \left\langle e^{-i k_1 (r(s_1) - r(s_3))} \right\rangle_W \left\langle e^{-i k_2 (r(s_2) - r(s_3))} \right\rangle_W \]

\[ = \int_0^1 ds_1 ds_2 ds_3 \left\langle e^{-i k_1 r(s_1) - i k_2 r(s_2)} \right\rangle_W \left\langle e^{i k_1 r(s_1) - i k_2 r(s_2)} \right\rangle_W \]

\[ \left| k_{\nu} = -k_{\alpha_1} \otimes s_{\alpha_1} - k_{\alpha_2} \otimes s_{\alpha_2} \right| \]

Finally, the fourth-order correlator is given by

\[ g_{\Psi^4}(k_1, k_2, k_3) = \int_0^1 ds_1 ds_2 ds_3 ds_4 \left\langle e^{-i \sum_{\nu=1}^4 k_{\nu} r(s_{\nu})} \right\rangle_W \]

\[ \left| k_{\nu} = -\sum_{\nu=1}^4 s_{\nu} \right| \]
a. *Lamellar case*

The third- and fourth-order correlators depend on the directions of the wave-vectors. In particular, we require the “lamellar” case, in which all wave-vectors are collinear. We note that \( g_3(k, -k) = g_D(k^2) \), and define the rescaled version of \( \omega \) small and large \( x \) asymptotic regimes of the scaling function \( \omega \), which is computed in [12] in the asymptotic regimes of small and large \( x \). For convenience, we define a rescaled version of \( \omega \),

\[
\omega(x) = \begin{cases} 
\omega_1(x) := 1 - 0.4409x^2 + 0.1316x^4 & \text{for } x \ll 1, \\
\omega_2(x) := 3\left(\frac{x^2}{8.1678}\right)^{1/4} e^{-\sqrt{x}/1.678} \\
\times \left(1 + \frac{27}{40\sqrt{2.1678x}}\right) & \text{for } x \gg 1.
\end{cases}
\]

In order to access the whole range of \( 0 < x < \infty \) we interpolate between the asymptotic regimes using the interpolating rational function

\[
\omega(x) \approx \begin{cases} 
\omega_1(x), & \text{for } x < \frac{1}{2}, \\
\omega_{ip}(x), & \text{for } \frac{1}{2} \leq x < 2, \\
\omega_2(x), & \text{for } x \geq 2,
\end{cases}
\]

with the interpolating rational function

\[
\omega_{ip} := \frac{b_0 + b_1 x}{1 + a_1 x + a_2 x^2 + a_3 x^3}.
\]

The coefficients \( a_1 = -0.055, a_2 = 0.165, a_3 = 0.139, b_0 = 1.023 \) and \( b_1 = -0.194 \) are chosen such that the value and first derivative of \( \omega_{ip}(x) \) coincide with those of \( \omega_1(x) \) at \( x = 1/2 \) and with those of \( \omega_2(x) \) at \( x = 2 \); an

\[
g_3(k^2) := g_3(k, k) = \frac{-(e^{-4k^2} - 1 + 4k^2 - 8k^4) + 64(e^{-k^2} - 1 + k^2 - \frac{1}{2}k^4)}{12k^6} = 1 - k^2 + \frac{2}{3}k^4 + O(k^6),
\]

\[
g_{\psi^2}(k^2) := g_{\psi^2}(k, -k) = \frac{-e^{-2k^2} + (8 + 2k^2)e^{-k^2} + 4k^2 - 7}{k^6} = 1 - \frac{2}{3}k^2 + \frac{17}{60}k^4 + O(k^6)
\]

and

\[
g_{\psi^4}(k^2) := g_{\psi^4}(k, k, -k) = \frac{144k^4 - 60k^2(9 + 4e^{-k^2}) + 784(1 - e^{-k^2}) - (1 - e^{-4k^2})}{18k^8} = 1 - \frac{2}{3}k^2 + \frac{11}{30}k^4 + O(k^4).
\]

**APPENDIX C: SCALING FUNCTION FOR THE GELATION ORDER PARAMETER**

The localization lengths \( \tau \) of monomers in the gel fraction of a crosslinked homopolymer melt or blend are distributed according to the distribution \( p(\tau) \); see section [13]. The fraction of the gel and the distribution are determined from the self-consistent solution of the saddle-point equations with the order parameter hypothesis (21). The gelation order parameter, essentially the Laplace transform of \( p(\tau) \), is proportional to a scaling function \( \omega(x) \), which is computed in [13] in the asymptotic regimes of small and large \( x \). For convenience, we define a rescaled version of \( \omega \),

\[
w(k^2) := 2 \cdot \omega\left(\sqrt{8k^2/3}\right), \quad (C1)
\]

This also absorbs a factor of two arising from the different length-scale used in [12] (the Wiener Hamiltonian used therein differs by a factor of two).

1. *Interpolation formula*

The scaling function \( \omega(k) \) defined in [12] can be described asymptotically by

\[
\omega(x) \approx \begin{cases} 
\omega_1(x), & \text{for } x \ll 1, \\
\omega_2(x), & \text{for } x \gg 1.
\end{cases}
\]

In order to access the whole range of \( 0 < x < \infty \) we interpolate between the asymptotic regimes using the interpolation formula

\[
\omega(k) \approx \begin{cases} 
\omega_1(x), & \text{for } x < \frac{1}{2}, \\
\omega_{ip}(x), & \text{for } \frac{1}{2} \leq x < 2, \\
\omega_2(x), & \text{for } x \geq 2,
\end{cases}
\]

with the interpolating rational function

\[
\omega_{ip} := \frac{b_0 + b_1 x}{1 + a_1 x + a_2 x^2 + a_3 x^3}.
\]
additional sampling point is the numerical value $\omega(x = 1) = 0.664$.

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