

## Glassy states and microphase separation in cross-linked homopolymer blends

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**Abstract.** – The physical properties of blends of distinct homopolymers, cross-linked beyond the gelation point, are addressed via a Landau approach involving a pair of coupled order-parameter fields: one describing vulcanisation, the other describing local phase separation. Thermal concentration fluctuations, present at the time of cross-linking, are frozen in by cross-linking, and the structure of the resulting glassy fluctuations is analysed at the Gaussian level in various regimes, determined by the relative values of certain physical length scales. The enhancement, due to gelation, of the stability of the blend with respect to demixing is also analysed. Beyond the corresponding stability limit, gelation prevents complete demixing, replacing it by microphase separation, which occurs up to a length scale set by the rigidity of the network, as a simple variational scheme reveals.

*Introduction.* – Molten blends of distinct homopolymers have a strong tendency to phase separate, compared with unpolymerised mixtures, due to the fact that their entropy of mixing is reduced by a factor of the degree of polymerisation. Random permanent cross-linking hampers the demixing process, and completely inhibits macroscopic phase separation, provided enough cross-links are introduced to cause the blend to undergo a transition to a gel. de Gennes [1] was the first to point out that the region of compatibility (*i.e.* the region in which the melt remains mixed) is substantially increased by cross-linking, and that instead of macroscopic phase separation, the gel undergoes microphase separation (MPS) with a domain size comparable to the typical mesh size of the random macromolecular network.

de Gennes' predictions were subsequently confirmed in scattering experiments [2]. However, a discrepancy remained, concerning the scattering intensity at small wave numbers. Whereas de Gennes predicted a *vanishing* intensity at zero wave number, via an analogy with the polarisation of a dielectric medium, the experiments showed a *non-vanishing* intensity. Several modifications of the de Gennes theory have been proposed. Benmouna *et al.* [3] suggest that the discrepancy arises through the neglect of concentration fluctuations, which are present during the cross-linking process and are “frozen in” by the cross-linking process. These authors introduce a screening length, self-consistently, by assuming that the scattering intensity at zero wave number is not changed by cross-linking. Read *et al.* [4] instead suggest a microscopic model for the gel, in which each chain is anchored at its ends to fixed random points in space. By using reasonable assumptions for the distribution of the quenched end-to-end vectors, they

arrive at an intensity similar to that of ref. [3], and also investigate effects of applied strain. Simulations by Lay *et al.* [5] reveal rather large cooperative rearrangements of the network upon MPS, allowing for domain sizes larger than the radius of gyration of the network strands.

In this letter we focus on “charge” fluctuations in gels that have been prepared from blends in a homogeneously mixed state, characterised by a sufficiently small Flory incompatibility parameter. By “charge” we mean the difference between the local densities of the two species of homopolymer. We concentrate on two themes:

- To what extent do the charge fluctuations present during cross-linking become frozen-in in the gel phase? This is particularly interesting if the cross-linking is performed close to phase separation, so that fluctuations are present up to a very large length scale, which can be either smaller or larger than the localisation length scale characterising the gel.
- How do frozen-in charge fluctuations affect the scattering intensity and MPS? To what extent does gelation enhance the stability of the mixed state, and to what extent can one characterise the MPS state that emerges at large enough incompatibility parameter?

Our starting point is a Landau expansion for the free energy in terms of *two* order parameter fields: the local charge fluctuations associated with phase separation, and the local static density fluctuations associated with the gelation transition. This free energy can be derived from a microscopic model [6], extending previous work on the gelation transition [7] to include the incompatibility of homopolymer blends. In this letter we do not dwell upon the derivation of the Landau free energy, but rather work out its consequences. As we shall see, the phase diagram is controlled by three parameters: the cross-link density control parameter  $\mu$ , and the incompatibilities at cross-linking  $\chi_p$  and at measurement  $\chi_m$  ( $p$  stands for *preparation*, and  $m$  for *measurement*).

The Landau free energy allows us to compute the frozen-in charge fluctuations without any *ad hoc* assumptions. We show that there are competing length scales: in a strong gel, the fluctuations are frozen-in almost completely, and hence preserve the native length scale at cross-linking; in a weak gel, by contrast, the charge fluctuations are only partially frozen in, limited by the length scale characterising localisation in the gel. We calculate the modification of the range of compatibility due to cross-linking, in terms of the gel order parameter, and discuss the scattering intensity in the gel, including the region in which MPS is approached. With the aim of developing a rough picture of the MPS state itself, we also analyse a lamellar-state Ansatz for the MPS state beyond, but close to, the transition.

*Model.* – We consider a blend of two incompatible homopolymer species, “A” and “B”. The two species are modelled identically as Gaussian chains of length  $L$ , and the blend is taken to contain  $N/2$  chains of each type. The mutual repulsion is modelled by the interaction

$$H^X = -\frac{\chi V}{2N} \sum_{a,a'=A,B} (2\delta_{a,a'} - 1) \sum_{i,i'=1}^{N/2} \int_0^1 ds \int_0^1 ds' \delta(\mathbf{r}_i^a(s) - \mathbf{r}_{i'}^{a'}(s')), \quad (1)$$

where  $\mathbf{r}_i^a(s)$  denotes the position of the monomer at arclength  $s$  on chain  $i$ , which can be either of type A ( $a = A$ ) or B ( $a = B$ ). The strength of the repulsion is controlled by the incompatibility, *i.e.*, the Flory-Huggins parameter  $\chi$ . On cooling, the un-cross-linked melt would undergo a second-order phase transition at  $T/\chi = 1$  from a homogeneously mixed phase to a phase-separated state. In the following, we choose units such that  $k_B T = 1$ . Since there is no other relevant energy scale, we shall refer to  $\chi$  as the inverse temperature. The

order parameter for a general phase-separation transition is given by the local imbalance in the concentration of  $A$  and  $B$  monomers (which we are referring to as charges):

$$\Psi(\mathbf{k}) = \frac{1}{N} \sum_{a=A,B} \sum_{i=1}^{N/2} \int_0^1 ds (\delta_{a,A} - \delta_{a,B}) \langle e^{i\mathbf{k} \cdot \mathbf{r}_i^a(s)} \rangle. \quad (2)$$

In the homogeneous state, the expectation value of the order parameter vanishes:  $\Psi(\mathbf{k}) = 0$ . If two homogeneous phases coexist,  $\Psi(\mathbf{r}) = \pm\Psi_0 \neq 0$  deep within either of them. For microphase separation we expect  $\Psi(\mathbf{k}) \neq 0$  for the nonzero  $\mathbf{k}$ 's characterising, *e.g.*, a striped state.

The cross-links are taken to connect randomly chosen pairs of monomers, without regard to their type, except for the intrinsic charge correlations present in the un-cross-linked blend. Hence, we use the Deam-Edwards distribution [8] to average over the quenched connectivity. As a function of the amount of cross-linking, the system undergoes a gelation transition from a viscous fluid to an amorphous solid at  $\mu_c = 1$  [7]. The order parameter for the gelation transition comprises the ( $g \geq 2$ ) moments of the local density fluctuations:

$$\Omega(\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_g) = \frac{1}{N} \sum_{a=A,B} \sum_{i=1}^{N/2} \int_0^1 ds \left[ \langle e^{i\mathbf{k}_1 \cdot \mathbf{r}_i^a(s)} \rangle \dots \langle e^{i\mathbf{k}_g \cdot \mathbf{r}_i^a(s)} \rangle \right], \quad (3)$$

and these acquire nonzero values in the gelled state, provided that  $\mathbf{k}_1 + \mathbf{k}_2 \dots + \mathbf{k}_g = \mathbf{0}$ . This condition is a consequence of the macroscopic translational invariance (MTI) of the emerging amorphous solid, which of course enforces the MTI of the density itself:  $\Omega(\mathbf{k}_1) = 0$ . In our model, this homogeneity is ensured by a sufficiently strong excluded-volume interaction. The thermal average is denoted by  $\langle \dots \rangle$ , and the quenched average over the cross-links by  $[\dots]$ .

*Landau free energy.* – Averaging over the quenched random cross-links with the help of the replica technique gives rise to a Landau free energy  $f = \lim_{n \rightarrow 0} f_n$  in terms of the replicated order parameters:

$$2nf_n(\{\Psi, \Omega\}) = \overline{\sum_{\hat{k}} \left( \frac{1}{\mu} - g_D(|\hat{k}|) \right) |\Omega(\hat{k})|^2} - \frac{1}{3} \overline{\sum_{\hat{k}_1, \hat{k}_2, \hat{k}_3} \delta_{\hat{k}_1 + \hat{k}_2 + \hat{k}_3, \hat{0}} \Omega(\hat{k}_1) \Omega(\hat{k}_2) \Omega(\hat{k}_3)} + \sum_{\alpha=0}^n \sum_{\mathbf{k}}' \left( \frac{1}{\chi^\alpha} - g_D(|\mathbf{k}|) \right) |\Psi^\alpha(\mathbf{k})|^2 - \sum_{\alpha \neq \beta} \sum_{\mathbf{k}_1, \mathbf{k}_2}' \Psi^\alpha(\mathbf{k}_1) \Psi^\beta(\mathbf{k}_2) \Omega(-\mathbf{k}_1 \hat{e}^\alpha - \mathbf{k}_2 \hat{e}^\beta) + \dots \quad (4)$$

To simplify the notation, we have introduced  $(n + 1)$ -times replicated wave vectors  $\hat{k} = (\mathbf{k}_0, \mathbf{k}_1, \dots, \mathbf{k}_n) = \sum_{\alpha=0}^n \mathbf{k}_\alpha \hat{e}^\alpha$ , which can be expanded in a complete orthonormal basis  $\{\hat{e}^\alpha\}_{\alpha=0}^n$  in replica space. The symbols  $\sum_{\mathbf{k}}'$  and  $\overline{\sum_{\hat{k}}}$  denote summations excluding the terms  $\mathbf{k} = \mathbf{0}$  and  $\hat{k} = \mathbf{k} \hat{e}^\alpha$ . The Debye function is given by  $g_D(k) \equiv 2(e^{-k^2} - 1 + k^2)/k^4$ , and all wave numbers have been made dimensionless with the radius of gyration  $R_g^2 = La^2/2d$  of a single chain, with  $d$  being the dimensionality of space. In general, the homopolymer blend is cross-linked at one temperature,  $\chi_p^{-1}$ , and measurements are performed at a distinct temperature,  $\chi_m^{-1}$ . In the replica formalism this is encoded in  $\chi^\alpha = (\chi_p, \chi_m, \dots, \chi_m)$ .

As a first step, we apply the *saddle point* approximation to eq. (4) in the range of parameters  $\chi_p < 1$ ,  $\chi_m < 1$  and  $\mu > 1$ , so that  $\bar{\Psi} = 0$ , whereas the order parameter for the gel [9, 10] acquires a nonzero value:

$$\bar{\Omega}(\hat{k}) = \delta_{\hat{k}, \mathbf{0}} Q \int_0^\infty d\tau \pi(\tau) \exp \left[ -\hat{k}^2 \xi_1^2 / 2\tau \right] \approx \delta_{\hat{k}, \mathbf{0}} \cdot \xi_1^{-2} w \left( |\hat{k}| \xi_1 / \sqrt{2} \right). \quad (5)$$

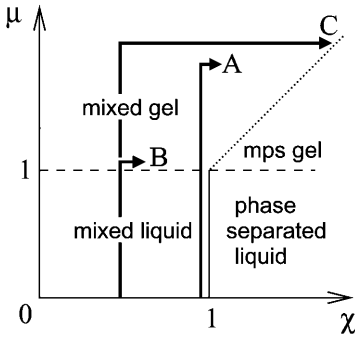


Fig. 1

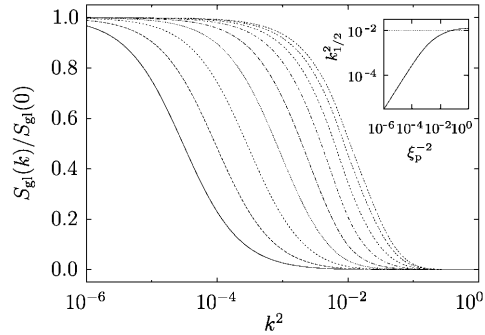


Fig. 2

Fig. 1 – Phase diagram of the polymer blend in the  $(\chi, \mu)$ -plane. The state of the system is, however, history dependent (see text for details).

Fig. 2 – Disorder-averaged  $S_{gl}(k)/S_{gl}(0)$  vs.  $k^2$  for  $\chi_m = 0.1$ ,  $\xi_1^2 = 10^2$ , and  $\xi_p^2 = 10^5, 10^{4.5}, \dots, 10^1$  (from left to right). Inset: half-width  $k_{1/2}^2$ , crossing over from  $\xi_p^{-2}$  to  $\xi_1^{-2}$  (horizontal line).

A nonzero fraction  $Q$  of particles is localised with a broad distribution of localisation lengths, expressed in terms of a scaling function  $\pi(\tau)$ . The typical localisation length  $\xi_1$  is given by the distance  $\xi_1^{-2} = \mu - 1$  from the gelation transition. Macroscopic translational invariance is guaranteed by the Kronecker- $\delta$  factor, enforcing  $\vec{k} \equiv \sum_{\alpha} \mathbf{k}_{\alpha} = \mathbf{0}$ . The scaling function  $w(x)$  is related to that defined in [7] via  $w(x) \equiv 2 \cdot \omega(\sqrt{4/3} \cdot x)$ .

*Stability of the homogeneously mixed state.* – Next, we consider charge fluctuations and study stability with respect to phase separation with the help of the Hessian matrix,

$$A_{\alpha,\beta}(k) \equiv \delta_{\alpha,\beta}(\chi_{\alpha}^{-1} - g_D(k)) - (1 - \delta_{\alpha,\beta}) \xi_1^{-2} w(k\xi_1), \quad (6)$$

obtained by expanding eq. (4) about the saddle point. In the limit  $n \rightarrow 0$ , the eigenvalues of  $A$  are given by  $\lambda_1(k) = \chi_p^{-1} - g_D(k)$  and  $\lambda_2(k) = \chi_m^{-1} - g_D(k) + \xi_1^{-2} w(k\xi_1)$ . The first eigenvalue,  $\lambda_1$ , is not degenerate and is always positive, as we assume that cross-linking takes place in the homogeneously mixed state. The second eigenvalue,  $\lambda_2$ , is  $n$ -fold degenerate and vanishes at  $\chi_{crit} = 1 + 1.38 \xi_1^{-2}$  at the nonzero wave number  $k_{crit}^2 = 1.78 \xi_1^{-2}$ . (These results were derived from the Landau expansion, and hence are systematic only to lowest order in  $\xi_1^{-2}$ .) We conclude that the range of temperatures  $\chi_m < \chi_{crit}$  in which the gel is stable with respect to phase separation is enlarged, compared to the un-cross-linked polymer blend, as one would expect, because cross-links hinder the demixing process. In this temperature range there are, however, frozen-in charge fluctuations, which we shall discuss next. Later, we shall discuss the instability with respect to MPS that occurs when  $\chi_m$  approaches  $\chi_{crit}$  from below.

*Phase diagram.* – A schematic phase diagram in the  $(\chi_m, \mu)$ -plane is shown in fig. 1. We restrict the discussion to gels prepared from a homogeneous liquid ( $\chi_p < 1$ ) by instantaneous cross-linking. Once the gel is prepared at a given value of  $\chi_p$  and a given  $\mu$ , only the incompatibility  $\chi_m$  may be varied. The line  $\mu = 1$  (dashed) separates the gel and the liquid state, which is divided into a mixed phase and a macrophase separated liquid by  $\chi = 1$  (solid line). The line  $\chi_m = \chi_{crit}$  (dotted) separates the mixed gel from the microphase separated one. The transition lines are independent of  $\chi_p$ . The properties of the sample depend on its history, and we have indicated two representative *paths*, specified by the values of  $\mu$ ,  $\chi_p$  and  $\chi_m$ ; here, we use the  $\chi$ -axis for *both*,  $\chi_p$  (vertical part of the path) and  $\chi_m$  (end point). Path A refers to

a gel prepared close to macroscopic phase separation, path  $B/C$  refers to a gel prepared well in the mixed state. At point  $B$ , cross-linking is stopped just beyond the gelation threshold, whereas point  $C$  is reached by cross-linking well into the gel phase and approaching MPS.

*Charge glass.* – Within the Gaussian expansion around the saddle point, charge fluctuations are determined by the Hessian according to  $\langle \Psi^\alpha(\mathbf{k}) \Psi^\beta(-\mathbf{k}) \rangle = (A^{-1}(k))_{\alpha,\beta}$ . In particular, glassy correlations are detected by a non-zero off-diagonal propagator:

$$S_{\text{gl}}(k) = [\langle \Psi(\mathbf{k}) \rangle \langle \Psi(-\mathbf{k}) \rangle] = \frac{\xi_1^{-2} w(k\xi_1) (\chi_p^{-1} - g_D(k) + \xi_1^{-2} w(k\xi_1))}{(\chi_p^{-1} - g_D(k)) \lambda_2^2(k)}. \quad (7)$$

To discuss these fluctuations, one should note that there are three competing length scales: The typical localisation length  $\xi_1$  of the gel, determined by the distance to the gelation threshold; the correlation length  $\xi_p$  of the preparation ensemble, given by the distance  $\xi_p^{-2} = 1 - \chi_p$  to the demixing transition *before* cross-linking; and  $\xi_m$ , corresponding to the distance  $\xi_m^{-2} = \chi_{\text{crit}} - \chi_m$  to the microphase separation line.

If  $\xi_p \gg (\xi_1, \xi_m)$ , the gel is prepared close to macroscopic phase separation, corresponding to path  $A$  in fig. 1. The thermal charge fluctuations present before cross-linking are very long-ranged, and are almost completely frozen in by the network. In this regime, eq. (7) reduces to  $S_{\text{gl}}(k) \sim (\xi_p^{-2} + k^2/3)^{-1}$ , and the glassy correlations decay on the scale  $k \sim \xi_p^{-1}$ , given by the fluctuations of the *preparation ensemble*.

If  $\xi_1 \gg (\xi_p, \xi_m)$ , *i.e.* in a weak gel (path  $B$ ), the network is rather wide-meshed, which limits the preservation of fluctuations to the inverse localisation length  $\xi_1^{-1}$ . In this limit, the glassy correlations are approximately given by  $S_{\text{gl}}(k) \sim w(k\xi_1)/\xi_1^2$ , and decay on the scale  $k \sim \xi_1^{-1}$ .

The cross-over between these scales is demonstrated in fig. 2, which shows  $S_{\text{gl}}(k)/S_{\text{gl}}(0)$  far from MPS for  $\xi_1 = 10$ . For the leftmost curve  $\xi_p^2 = 10^5 \gg \xi_1^2 = 100$ , and hence the decay occurs at  $k \sim \xi_p^{-1}$ . Upon decreasing  $\xi_p$  the curves are shifted to the right, until for  $\xi_1 \gg \xi_p$  the decay is determined by  $\xi_1$ . The inset shows the half-width  $k_{1/2}^2$  at half-maximum of  $S_{\text{gl}}(k)$ , first growing linearly with  $\xi_p^{-2}$ , then saturating at  $\xi_p^{-2}$  (horizontal line).

Close to microphase separation (path  $C$ ), the glassy correlations are dominated by critical fluctuations on the scale  $k \approx k_{\text{crit}} \sim \xi_1^{-1}$  and ultimately diverge at microphase separation.

*Scattering function.* – The scattering intensity is determined by the diagonal correlations

$$S(k) + \chi_m = [\langle \Psi(\mathbf{k}) \Psi(-\mathbf{k}) \rangle] = \lambda_2^{-1}(k) + \frac{\xi_1^{-2} w(k\xi_1) (\chi_p^{-1} - g_D(k) + \xi_1^{-2} w(k\xi_1))}{\lambda_2^2(k) (\chi_p^{-1} - g_D(k))}. \quad (8)$$

We expect two main contributions to  $S(k)$ : The fluctuations that are present at cross-linking and frozen-in in the gel, are characterised by small wave numbers, being the precursor of a homogeneous phase separation. The fluctuations that signal MPS, on the other hand, are dominant at  $k \sim \xi_1^{-1}$ .

If  $\xi_p \gg (\xi_1, \xi_m)$ , *i.e.* a gel prepared close to phase separation (path  $A$ ), the network preserves the strong fluctuations that were present before gelation, giving a large contribution at small wave vectors up to  $k \sim \xi_p^{-1}$ .

If  $\xi_m \gg (\xi_1, \xi_p)$ , *i.e.* measurement close to MPS (path  $C$ ), the fluctuations towards microphase separation grow large, giving rise to a peak in the scattering function at  $k \approx k_{\text{crit}} \sim \xi_1^{-1}$ . At the critical point of MPS, the scattering function diverges like  $S(k) \sim \lambda_2^{-2}(k)$ .

The contributions of both regimes can be seen in fig. 3. Panel (a) shows  $S(k)$  for a fixed distance  $\xi_m^{-2}$  from the MPS transition with  $\xi_p^{-2}$  decreasing towards (pre-cross-linking) phase separation. We observe increasingly stronger weight to  $S(k)$  at small wave numbers.

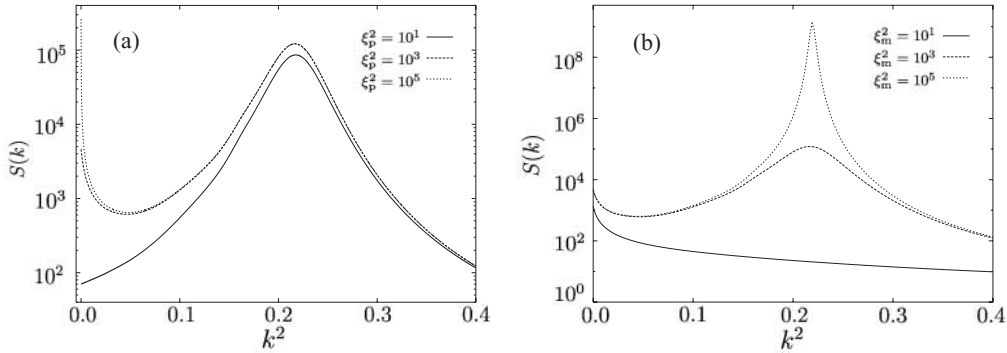


Fig. 3 – Scattering function  $S(k)$  vs.  $k^2$  showing weight at  $k = 0$  due to frozen-in fluctuations and at  $k^2 \sim 1.8 \xi_1^{-2}$  when approaching microphase separation. (a)  $\xi_1^2 = 10^1$ ,  $\xi_m^2 = 10^3$ , several values of  $\xi_p^2$  (see legend). (b)  $\xi_1^2 = 10^1$ ,  $\xi_p^2 = 10^3$ , several values of  $\xi_m^2$  (see legend).

Panel (b) shows  $S(k)$  at a fixed distance  $\xi_p^{-2}$  from phase separation before cross-linking. Upon decreasing the distance  $\xi_m^{-2}$  to MPS, the scattering function  $S(k)$  is dominated more and more by fluctuations at  $k_{\text{crit}}$ .

If  $\xi_1 \gg (\xi_p, \xi_m)$ , *i.e.* in a weak gel (path B), the frozen-in fluctuations are small on all length scales. Hence, the scattering function is dominated by purely thermal fluctuations, seemingly towards macroscopic demixing, because the gel is too weak to severely restrict phase separation on the length scale  $\xi_m$ . In this limit, eq. (8) reduces to  $S(k) = \xi_m^{-2} + k^2/3$ , which decays on a scale  $k \sim \xi_m^{-1}$  and is shown as the lowest curve in fig. 4. Decreasing the distance to the (pre-gelation) phase separation point,  $\xi_p^{-2}$ , we observe the build-up of intensity at small wave numbers (panel a). Decreasing the distance to microphase separation,  $\xi_m^{-2}$ , leads to an increasingly stronger peak at  $k_{\text{crit}}^2 \approx 1.78 \xi_1^{-2}$  (panel b).

Similar precursors of MPS also occur in the scattering function of *diblock copolymer melts* [11], yet on a different length scale: the radius of gyration of the blocks instead of the localisation length of the gel. Furthermore, the scattering function of diblock copolymers vanishes at  $k = 0$  due to the absence of frozen-in fluctuations.

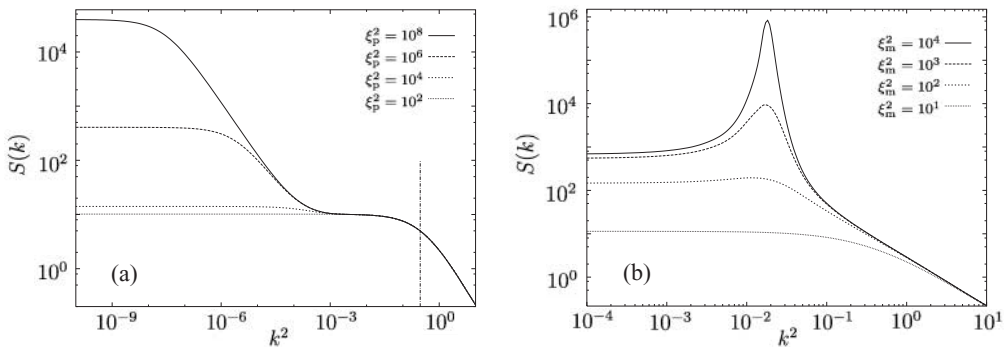


Fig. 4 – Scattering function  $S(k)$  vs.  $k^2$  showing weight at small  $k$  due to thermal and frozen-in fluctuations and at  $k^2 \sim 1.8 \xi_1^{-2}$  when approaching microphase separation. (a)  $\xi_1^2 = 10^3$ ,  $\xi_m^2 = 10^1$ , several values of  $\xi_p^2$  (see legend). Vertical line:  $k^2 = 3 \xi_m^2$ . (b)  $\xi_1^2 = 10^2$ ,  $\xi_p^2 = 10^1$ , several values of  $\xi_m^2$  (see legend).

*Microphase separation.* – The analysis of the microphase separated state requires supplementing the Landau expansion (4) by fourth-order terms. To minimise this free energy variationally, we consider a simple, replica-symmetric, lamellar microphase state:

$$\Psi_{\mathbf{k}}^{\alpha} = \begin{cases} 0, & \text{for } \alpha = 0, \\ \sqrt{2} (\delta_{\mathbf{k},\mathbf{q}} + \delta_{\mathbf{k},-\mathbf{q}}) \bar{\Psi}, & \text{otherwise.} \end{cases} \quad (9)$$

Note that, because the melt is cross-linked in the homogeneously mixed state ( $\chi_p < 1$ ), the zeroth replica is treated separately. Inserting the Ansatz (9) into the fourth-order expansion of the free energy we obtain

$$\lim_{n \rightarrow 0} f_n(\bar{\Psi}, q) = 2\lambda_2(q) \bar{\Psi}^2 + g_4(q) \bar{\Psi}^4, \quad (10)$$

where  $g_4(q) = 1 - \frac{2}{3}q^2 + \mathcal{O}(q^4)$  denotes a Debye-like vertex function. Minimisation with respect to both the amplitude  $\bar{\Psi}$  and the wave number  $q$  yields

$$\bar{\Psi}^2 \sim \chi_m - \chi_{\text{crit}} \quad \text{and} \quad q_{\text{opt}}^2 - k_{\text{crit}}^2 \sim \chi_m - \chi_{\text{crit}}. \quad (11)$$

We presume that the free energy would be lowered further in a state that is not characterised simply by a single wave vector, as above; instead the direction of the wave vector should vary locally to adjust to the random static charge fluctuations induced by the cross-links.

It may be that the MPS transition is rendered first order by fluctuations, as in the case of diblock copolymer melts [12].

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## REFERENCES

- [1] DE GENNES P. G., *J. Phys. (Paris) Lett.*, **40** (1979) L-69.
- [2] BRIBER R. M. and BAUER B. J., *Macromolecules*, **21** (1988) 3296.
- [3] BENMOUNA M., VILGIS T. A., DAOUD M. and BENHAMOU M., *Macromolecules*, **27** (1994) 1172; BETTACHY A., DEROUICHE A., BENHAMOU M. and DAOUD M., *J. Phys. I*, **1** (1991) 153; BETTACHY A., DEROUICHE A., BENHAMOU M., BENMOUNA M., VILGIS T. A. and DAOUD M., *Macromol. Theory Simul.*, **4** (1995) 67.
- [4] READ D. J., BRERETON M. G. and MCLEISH T. C. B., *J. Phys. II*, **5** (1995) 1679.
- [5] LAY S., SOMMER J.-U. and BLUMEN A., *J. Chem. Phys.*, **113** (2000) 11355.
- [6] WALD C., ZIPPELIUS A. and GOLDBART P. M., in preparation (2005).
- [7] GOLDBART P. M., CASTILLO H. E. and ZIPPELIUS A., *Adv. Phys.*, **45** (1996) 393.
- [8] DEAM R. T. and EDWARDS S. F., *Proc. Trans. R. Soc. London, Ser. A*, **280** (1976) 317.
- [9] CASTILLO H. E., GOLDBART P. M. and ZIPPELIUS A., *Europhys. Lett.*, **28** (1994) 519.
- [10] PENG W., CASTILLO H. E., GOLDBART P. M. and ZIPPELIUS A., *Phys. Rev. B*, **57** (1998) 839.
- [11] LEIBLER L., *Macromolecules*, **13** (1980) 1602.
- [12] BRAZOVSKIĀ S. A., *Zh. Eksp. Teor. Fiz.*, **68** (1975) 85; FREDRICKSON G. H. and HELFAND E., *J. Chem. Phys.*, **87** (1987) 697.