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Effects of inhomogeneities of cross-links on a microphase separation of polymer mixtures

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Abstract. — We generalize de Gennes' theory of the microphase separation of cross-linked polymer mixtures to take into account the spatial fluctuations of the elasticity constant c , preventing the mixture from complete segregation. Within a mean-field analysis we found that the spatial fluctuations of $c(\mathbf{r})$, which are assumed to obey the Poisson distribution, enlarge the size of the domains. The latter is obtained to be temperature dependent.

The microphase separation in polymer systems such as block copolymers [1-3], cross-linked polymers [4, 5], interpenetrating networks [6-8] are of current interest in the literature. Two chemically different polymers A and B being not compatible do not completely segregate because they are kept together by cross-links, but can segregate on some scale $r^* \sim 2\pi/q^*$. de Gennes [4] proposed a description of the microphase separation based on the electrostatic analogy. According to this idea the appearance of the nonzero value of the order parameter $\phi(r)$ (charge density) is accompanied by the local polarization $\mathbf{P}(\mathbf{r})$ representing the elastic forces due to the cross-links. The latter is connected with the charge density as follows

$$\text{div} \mathbf{P}(\mathbf{r}) = -\phi(\mathbf{r}). \quad (1)$$

The effective Hamiltonian (in units of kT) is given by $H = \int d^d r \mathcal{H}$, with $\mathcal{H}$

$$\mathcal{H} = \frac{1}{2}[(\chi_c - \chi)\phi(\mathbf{r})^2 + (a^2/24)(\nabla\phi(\mathbf{r}))^2 + c\mathbf{P}(\mathbf{r})^2] + \frac{u_0}{4}\phi(\mathbf{r})^4, \quad (2)$$

where χ is the Flory-Huggins interaction parameter, χ_c is its critical value at which the phase separation occurs. de Gennes estimated the elasticity constant c as $c \simeq 36/(n^2 a^2)$, with n being

the number of monomers between two consecutive cross-links and a the size of monomers. Here we consider the most symmetric case, i.e. parameters such as n and a being the same for both polymers A and B. In case of symmetric composition the ϕ^3 -term does not appear in (2). We note that the possibility for the appearance of the instability at a finite momentum was discussed already by Landau [9]. Brazovskii [10] elaborated the Landau theory to include the fluctuations.

In the present note we address the question of the effects of the inhomogeneities of the cross-links on the microphase separation. In this case the elastic constant c is supposed to be a random function of the position, i.e. $c \rightarrow c(\mathbf{r})$. This choice of the randomness differs from the choice $T_c \rightarrow T_c(\mathbf{r})$ considered extensively for standard phase transition problems [11]. There exist many possibilities for the realization of the inhomogeneities of cross-links. Here we will represent the inhomogeneities of cross-links by a Poisson distribution as follows

$$c(\mathbf{r}) = \bar{c} + c_0 \sum_{\mathbf{r}_i} v(\mathbf{r} - \mathbf{r}_i), \quad (3)$$

where $\mathbf{r}_i$ correspond to coordinates of particles randomly distributed in the volume of the system V and $v(\mathbf{r})$ is a function of $\mathbf{r}$ which will be identified as $c_0 \delta(\mathbf{r})$ with $\delta(\mathbf{r})$ being the Dirac delta-function. $\bar{c}$ is the nonfluctuating part of the elasticity constant. The average of $c(\mathbf{r})$ is $\bar{c} + c$, whereas the correlator of $c(\mathbf{r})$ is given by

$$\langle \Delta c(\mathbf{r}) \Delta c(\mathbf{r}') \rangle = c_0 c \delta(\mathbf{r} - \mathbf{r}'). \quad (4)$$

For spatial correlated cross-link density the delta-function in the right-hand side of (4) should be replaced by a function with some finite width. In case of weak disorder (small c_0) we expect that the effects are qualitatively the same as for the delta-correlated disorder.

We use the Poisson distribution because it guarantees that the elasticity constant cannot become negative. On the other hand this distribution gives a non zero probability that the elasticity constant be zero in some macroscopical volume. This probability being very small increases with increasing strength of fluctuations, c_0 . Therefore one should expect that the Poisson distribution may be relevant only for small strength of disorder c_0 . In this limit the distribution used goes over to the Gauss distribution, where the deviation of the elasticity constant from its average value is small. The applicability of the model based on the Poisson distribution can be extended to larger values of c_0 by introducing the term $\bar{c}$ in (3).

While it is well-known that the correct statistical average over frozen in disorder requires a "quenched average" [11], this is difficult to perform, and a first orientation over the problem often can be gained by the much simpler case of "annealed disorder". Physically this would mean the cross-links open and reconnect again. The annealed disorder can be relevant for interpenetrating networks, where the cross-links or at least a part of cross-links are simulated by entanglements, which can move along the chains. Due to the fact that some of the cross-links due to entanglements are mobile it is not clear that the fully quenched average is really closer to experimental situation. For simplicity only annealed average is considered in the following. The annealed average over $\mathbf{r}_i$ is carried out as follows

$$\begin{aligned} & \int d^d r_1 / V \dots \int d^d r_N / V \exp \left[-\frac{1}{2} \sum_{\mathbf{r}_i} \int d^d r P^2(\mathbf{r}) v(\mathbf{r} - \mathbf{r}_i) \right] \\ &= \left\{ \int d^d R / V \exp \left[-\frac{1}{2} \int d^d r P^2(\mathbf{r}) v(\mathbf{r} - \mathbf{R}) \right] \right\}^N \\ &= \exp \left\{ -\rho \int d^d R \left[1 - \exp \left(-\frac{1}{2} \int d^d r P^2(\mathbf{r}) v(\mathbf{r} - \mathbf{R}) \right) \right] \right\}, \end{aligned} \quad (5)$$

which results in the following effective Hamiltonian density

$$\mathcal{H}_{\text{eff}} = \frac{1}{2}(\chi_c - \chi)\phi^2 + \frac{1}{2}(a^2/24)(\nabla\phi)^2 + \frac{1}{2}\bar{c}P^2 + \rho \left(1 - e^{-(1/2)c_0P^2}\right) + \frac{1}{4}u_0\phi^4, \quad (6)$$

where ρ is the density of the particles which simulate the spatial fluctuations of $c(\mathbf{r})$ and we used $v(\mathbf{r}) = c_0\delta(\mathbf{r})$. The case considered by de Gennes [4] is obtained from (6) in the limit $c_0 \rightarrow 0$ and $c = \rho c_0 = \text{Cte}$ or $c_0 \rightarrow 0$ and $\rho = \text{Cte}$. The fluctuations of the elasticity constant being treated as annealed one in this paper are thought to be due by cross-links due to entanglements. It is not clear to what extent the fluctuations of the elasticity constant due to such moving cross-links can be described by a Poisson distribution. From the discussion given above it is expected that this may be the case only for small strength of fluctuations. The fluctuations due to moving cross-links are expected to be described more reasonably by the model (3), where $\bar{c}$ guarantees that the elasticity constant $c(\mathbf{r})$ cannot become zero. The mean field equation for the order parameter is obtained from (6) as follows

$$\delta H/\delta\phi(\mathbf{r}) = 0 \quad \text{or} \quad \delta H/\delta P(\mathbf{r}) = 0. \quad (7)$$

The mean field equation for the polarization in one dimension is

$$(\chi - \chi_c)P''(x) + (a^2/24)P^{\text{iv}}(x) + \bar{c}P(x) + cP(x)\exp(-\frac{c_0}{2}P^2(x)) - 3u_0P'(x)^2P''(x) = 0. \quad (8)$$

The mean-field equations (7, 8) are still difficult to be analyzed without approximations. We use the following approximate treatment of the Hamiltonian: $(\nabla\phi)^2 \rightarrow \phi^2/L^2$ and $P^2 \rightarrow \phi^2L^2$. Thus we only attempt a kind of dimensional analysis, with L being the length scale of the microphase separation, and ϕ the typical value of the order parameter in the domain of size L . We expect that the single scale approximation used here is reasonable in the vicinity of the critical point. Below and far from the critical temperature it would be necessary to introduce the scale corresponding to the interfacial width. The effective approximate Hamiltonian (6) is obtained as

$$\mathcal{H} = \frac{1}{2}(\chi_c - \chi)\phi^2 + \frac{1}{2}(a^2/24)L^{-2}\phi^2 + \frac{1}{2}\bar{c}L^2\phi^2 + \rho(1 - e^{-(1/2)c_0L^2\phi^2}) + \frac{1}{4}u_0\phi^4. \quad (9)$$

Minimizing this Hamiltonian with respect to the order parameter ϕ and the domain size L gives the following equations

$$\partial\mathcal{H}/\partial\phi = \phi(\chi_c - \chi + (a^2/24)L^{-2} + \bar{c}L^2 + cL^2e^{-(1/2)c_0L^2\phi^2} + u_0\phi^2) = 0, \quad (10)$$

$$\partial\mathcal{H}/\partial L = \phi^2(-(a^2/24)L^{-3} + \bar{c}L + cLe^{-(1/2)c_0L^2\phi^2}) = 0. \quad (11)$$

We note that the minimization procedure (10, 11) describes correctly the homogeneous case $c_0 \rightarrow 0$. The same mean-field treatment of the quenched version of the Hamiltonian (2) gives that the fluctuations of $c(\mathbf{r})$ are irrelevant, i.e. the results are the same as for $c(\mathbf{r}) = \text{Cte}$. This does not mean that there are no effects of the quenched disorder under consideration, because a careful treatment of the quenched case beyond mean field theory may be required.

Introducing instead of ϕ and L the variables $x = (1/2)c_0L^2\phi^2$ and $w = L/\bar{L}$, with $\bar{L} = (24(\bar{c} + c)/a^2)^{-1/4}$ being the length scale of the microphase separation in the homogeneous case, and supposing the inverse proportionality of χ on the temperature, we rewrite (10, 11)

as follows

$$w^2 \frac{T_c - T}{T_c - T_{mc}} \frac{T_{mc}}{T} = 1 + \frac{A}{2}x, \quad (12)$$

$$w = ((\bar{c} + c)/(\bar{c} + ce^{-x}))^{1/4}, \quad (13)$$

where $T_{mc} = T_c/(1 + 2(\bar{c} + c)\bar{L}^2/\chi_c)$ is the critical temperature of the microphase separation in the homogeneous case, and $A = 48u_0/(c_0a^2)$. In order that (12) and (13) correspond to the minimum of the Hamiltonian (9), the quadratic form $\delta^2\mathcal{H}$ should be positive definite. This gives the following conditions

$$A - B > 0, \quad (A - B)(2 - xB) - xB^2 > 0, \quad (14)$$

where $B = 1 - w^4u/(1 + u)$ with $u = \bar{c}/c$ was introduced. Thus in order to get the conditions on the microphase separation we should solve (12) and (13) by fulfilling the inequalities (14). We found that for temperatures $T > T_{mc}$ equations (12) and (13) do not have solutions.

In contrast to the case $\bar{c} = 0$ considered in [12], where a solution of (12) and (13) corresponding to a microphase separation exists only for small c_0 , for $\bar{c} \neq 0$ there exists always a solution of the above equations. Equations (12) and (13) can be solved perturbatively in powers of c_0 . Up to the first order in c_0 we get the domain size as follows

$$L/\bar{L} = 1 + \frac{1}{8} \frac{c}{\bar{c} + c} c_0 \bar{L}^2 (\chi - \chi_{mc})/u_0 + \dots \quad (15)$$

The latter shows that the size of microdomains L is temperature dependent and it increases with decreasing temperature. It follows from (15) that for small c_0 the size of the domains is influenced by the disorder correlator. It is expected that in the limit $c_0 \rightarrow 0$ (4) does not depend on the details of the distribution function of the disorder. In this limit we will obtain the same result if instead of the Poisson distribution we will use the Gauss distribution of the fluctuations with the correlator given by equation (4). The dependence of the domain size on the temperature obtained from the numerical solution of the equations (12) and (13) is shown in figure 1.

The temperature dependence of the domain size is the consequence of the annealed treatment of the fluctuations of $c(\mathbf{r})$, which again are thought to be caused by cross-links moving along the chains. An experimental observation of temperature dependence of the domain size should be interpreted in terms of the present theory as a consequence of cross-links due to entanglements. figure 2 shows the dependence of the order parameter $\phi/u_0^{1/2} \simeq (xA)^{1/2}/w$ on the temperature.

Near the critical temperature T_{mc} the order parameter behaves qualitatively in a similar way as that in de Gennes' theory. Away from T_{mc} the order parameter increases approximately linearly with decreasing temperature.

To conclude we have generalized de Gennes' theory of microphase separation in cross-linked polymer mixtures by taking into account the fluctuations of the elasticity constant which are assumed to obey a Poisson distribution. As de Gennes' theory the present one is also phenomenological. The main result of our mean-field analysis is that the fluctuations of the elasticity constant enlarge the size of the domains. The fluctuations of the elasticity constant are thought to be caused by cross-links moving along the chains. Such moving cross-links are caused by entanglements. This interpretation of the fluctuations of the elasticity constant seems to legitimate the annealed average of the latter. The temperature dependence of the size of domains obtained in the present model is the consequence of the annealed treatment of the fluctuations. The experimental verification of this dependence may give information on cross-links due to entanglements. The enlargement of the size of domains has been obtained in the experimental study [13]. The effect, however, is larger by an order of magnitude.

Fig. 1. — The dependence of the domain size on the temperature. The parameter u and A are shown in the inset.

Fig. 2. — The dependence of the order parameter on the temperature.

Since we have used two simplifying assumptions, namely the disorder average was treated as fully annealed rather than partially annealed, and also the full mean field equation (8) was replaced by approximate ones (Eqs. (10, 11)), the numerical predictions which follow from our treatment (Figs. 1, 2) are not necessarily very accurate. The development of a more reliable theory, which eliminates both of these shortcomings, would however not be straightforward.

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