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Kinetics of Microphase Separation in Interpenetrating Polymer Gels

The physical system considered here is an interpenetrating gel composed of two chemically different polymers, cross-linked in the high-temperature single-phase region. When the bath temperature is sufficiently lowered, below the usual critical temperature, the mixture tends to separate into two distinct phases; however, this does not occur, due to the permanent presence of cross-links. Below the spinodal temperature, a microphase separation takes place, accompanied by the appearance of microphase domains, contrary to the usual macrophase separation (in the absence of cross-links), where the phase domains are macroscopic.

This chapter summarizes the accomplishments in studying the kinetics of microphase separation in interpenetrating gels by a progressive reduction of the bath temperature. We particularly discuss the appearance of instabilities at the critical point. The chapter ends with a discussion on the effects of the presence of a good or a theta solvent, the initial composition fluctuations or charges in these kinetics.

1.1. Introduction

When the temperature is lowered, the polymer blends separately into two distinct phases, due to the chemical difference between the present species. This phase separation occurs even in the presence of a solvent. When the polymer chains are of high molar mass, the translational entropy is very small, and then, the chemical segregation between chemically different monomers is significantly amplified. In the temperature-composition phase diagram, a low or high critical separation temperature is then observed (de Gennes 1979a; Pincus 1981; Binder 1983) in

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certain cases. In the vicinity of this temperature, there are significant composition fluctuations, and there is a divergence in the correlation length that characterizes the spatial extent of these fluctuations.

Phase separation can be avoided by a chemical crosslinking of blend in the single-phase region to obtaining a gel termed *interpenetrating gel*. This gel can also be obtained by mixing, from the beginning, chemically different monomers and then initiating the polymerization process. In this case, the chemical cross-links are replaced by topological entanglements.

Naturally, when the temperature is reduced, the cross-linked polymer blend tends to separate in two phases, but the cross-links prevent the appearance of a macrophase separation, due to the elastic forces resulting from the presence of cross-links. As result of this competition, a microphase separation takes place (de Gennes 1979b; Binder and Frisch 1984; Battachy et al. 1991); this was theoretically studied for the first time by de Gennes (1979b) using a mean-field approach. The author has shown that the size of the microphase domains depends on the crosslinking rates and approximately corresponds to the average distance between two consecutive cross-links. A second important effect of cross-links is that it renders the polymer blend more compatible, and there is a deviation of the critical temperature that also depends on the cross-link density, defined as the number of cross-links per unit volume. Microphase separation in interpenetrating gels has been experimentally observed by Briber and Bauer (1988), who had used small-angle neutron scattering for the study of the structure of microphase domains in a cross-linked blend, which is composed of polystyrene and poly(vinyl methyl ether).

Let us consider an interpenetrating gel with high cross-link density. The typical distance scale of microphase separation is very small in comparison with the gyration-radius of uncross-linked polymer chains. Therefore, different kinetics are expected for non-cross-linked and cross-linked cases. The non-cross-linked polymer blends have been studied by de Gennes (1979a), Pincus (1981) and Binder (1983). They have shown that *reptation* of polymer chains has a significant contribution to the kinetics of phase separation. However, for cross-linked polymer blends, a small typical time scale is expected, since large-scale motions of cross-linked polymer chains are frozen by the presence of permanent cross-links. It can therefore be anticipated that, for the considered system, only Rouse motion is important. In this context, it had been shown that the dynamic structure factor of a polymer blend susceptible to phase separate can be decomposed in two modes (de Gennes 1981; Pincus 1981), namely a rapid mode, of low amplitude, and a low mode, of high amplitude. The first one corresponds to a local motion, while the second one is associated with a large-scale reptation of polymer chains. In a cross-linked system, above the freezing point, the reptation phenomenon is absent, because of constraints. This is why only a local motion of Rouse type is expected, which is essentially

responsible for the microphase separation kinetics. Rouse time corresponds to a motion occurring very early in the case of a non-cross-linked blend, which was discussed by the above-mentioned authors.

Section 1.2 reviews the main results concerning the static study (or at thermodynamic equilibrium) of the microphase separation. Section 1.3 is dedicated to the kinetic study of this microphase separation. Finally, in section 1.4, we discuss the results dealt with the kinetic study and compare them to those related to non-cross-linked blends.

1.2. Static study of microphase separation

Let us consider a blend made of two chemically different polymers, A and B. N denotes the common polymerization-degree of polymer-chains initially in the single-phase region of the phase diagram (high-temperature phase). The monomer composition is denoted by Φ. Due to the symmetry, $\Phi_c = 1/2$ is chosen as the critical monomer composition. Let us assume that the polymer chains are initially randomly distributed and there is no composition fluctuation. This is a high temperature approximation, which involves that the system is very far from its critical point. The blend is now strongly cross-linked, and by lowering the temperature, the interpenetrating gel is brought into the single-phase region. According to de Gennes (1979b), the free energy of such a system can be written, in a Landau approximation, as follows:

$$\frac{F[\phi]}{k_B T} = a^{-3} \int \left\{ (\chi_c - \chi)\, \phi^2(\vec{r}) + a^2 \left(\vec{\nabla}\phi(\vec{r}) \right)^2 + C\vec{P}^2(\vec{r}) \right\} d\vec{r} \qquad [1.1]$$

Here, χ denotes the Flory monomer–monomer interaction parameter, which is inversely proportional to temperature, $\chi_c = 2/N$ is the critical value of the interaction parameter of the non-cross-linked mixture, $\phi(\vec{r})$ is the local fluctuation of composition (or *order parameter*), defined by: $\phi(\vec{r}) = \Phi(\vec{r}) - \Phi_c$, where $\Phi(\vec{r})$ is the composition of a species of the non-cross-linked blend, a is the common size of monomers, k_B is the Boltzmann's constant and T is the absolute temperature of the cross-linked blend. There, the gradient term takes into account the local fluctuations of composition (Joanny 1978) and the last term, which is discussed below, is the elastic contribution due to cross-links. Critical parameters, $\chi_c = 2/N$ and $\Phi_c = 1/2$, are determined in the Flory–Huggins (FH) approximation (Flory 1953). It is important to note that relation [1.1] can be considered as the sum of the expansion of FH free energy in the vicinity of the critical point and the elastic term.

On the other hand, the resolution of equation [1.1] is equivalent to determining the effect of perturbations in the vicinity of the critical point. Previous studies on critical phenomena have shown that this effect can be either weak, causing a simple perturbation, or dramatic, leading to a change in the universality class of the problem. This will be the case in what follows.

The elastic contribution in equation [1.1] was introduced by de Gennes (1979b) by analogy with the polarization of a dielectric medium. The quantity C is the *rigidity constant* that was linked to the number, n, of monomers between two consecutive cross-links. According to de Gennes (1979b), its expression is given as:

$$C \cong n^{-2} \qquad [1.2]$$

In expression [1.1] of FH free energy, $\vec{P}$ is the *displacement vector* between the centers of mass of two strands A and B (a strand is the segment of a polymer chain between two neighboring cross-links). The polarization in the problem of the dielectric medium is equivalent to the distance between the centers of mass of various strands in the problem of polymer, and the charge fluctuations corresponding to the composition fluctuations. This involves that the quantities $\vec{P}$ and ϕ are not independent to each other, but linked by: $div\,\vec{P} = -\phi$, or in the reciprocal space, by:

$$i\vec{q}.\vec{P}(q) = -\phi(q) \qquad [1.3]$$

We are therefore led to consider only the longitudinal modes, and the free energy can be written as follows:

$$\frac{F[\phi]}{k_B T} = \sum_{\vec{q}} \left\{ (\chi_c - \chi) + q^2 + \frac{C}{q^2} \right\} \left| \phi_q \right|^2 \qquad [1.4]$$

Here, ϕ_q is the Fourier transform of the composition fluctuation:

$$\phi_q = \int \left[\boldsymbol{\Phi}(\vec{r}) - \boldsymbol{\Phi}_c \right] e^{i\vec{q}.\vec{r}}\, d\vec{r} \qquad [1.5]$$

The scattered intensity (or structure factor), $S(q)$, in a light or neutron scattering, is given as:

$$S(q) = \left\langle \left| \phi_q \right|^2 \right\rangle = \frac{1}{(\chi_c - \chi) + q^2 + \dfrac{C}{q^2}} \qquad [1.6]$$

It has a maximum for:

$$q^* = C^{1/4} \cong n^{-1/2} \quad [1.7]$$

The value of the scattering intensity at this maximum diverges at spinodal for:

$$\chi_c - \chi_s \cong -C^{1/2} \cong -n^{-1} \quad [1.8]$$

This deviation varies as the inverse of cross-links dose, n. Therefore, a divergence occurs for a non-zero value of the modulus of the transfer wave-vector, q, and this can be interpreted as a microphase separation. Then, there is a deviation of the critical temperature; the cross-linked system is more miscible than the non-cross-linked one.

The following section focuses on the study of kinetics of microphase in interpenetrating gels.

1.3. Kinetic study of microphase separation

As mentioned above, the main difference between demixing of a non-cross-linked polymer blend and a highly cross-linked polymer blend is that the distance scales being examined are highly different. Indeed, in the first case, the motions of polymer chains, at long distance, are controlled by reptation, while in the second case, there are local arrangements, over distances of the order of the size of microphase domains.

For a non-cross-linked polymer blend, de Gennes (1981) and Pincus (1981) have shown that the time dependence of the scattered intensity is the sum of *two* contributions. The first one is a rapid mode and it corresponds to a local reptation. The second having a high amplitude and being slower corresponds to a long distance reptation of the polymer chains and causes a disentanglement of species. In the present case, due to the permanent presence of cross-links, the latter should not be expected to bring their contribution, and longtime motions are then frozen. Local dynamics was not considered in the previous works, as it corresponds to kinetics during the first instants of the phase separation of blend. It is the only motion that is present here. It is the local Rouse dynamics that occur inside a tube formed by the other chains (de Gennes 1979a; Doi and Edwards 1986). This will appear in the expressions of Onsager coefficient that will be introduced below. Formally, we write equations similar to those related to a non-cross-linked blend (de Gennes 1980). More precisely, what we are looking for is the time evolution of the fluctuation at fixed wave-vector modulus, q. For this, the standard procedure that was thoroughly

discussed by Binder (1983) is applied. This time evolution can be found by introducing a current, $\vec{j}$, for species A. The continuity equation is given as:

$$\frac{\partial \Phi}{\partial t} + div\vec{j} = 0 \qquad [1.9]$$

Here, t represents the time parameter. The current $\vec{j}$ is linked to a chemical potential, $\mu(\vec{r}) = \partial F / \partial \Phi(\vec{r})$, by the following relation:

$$\vec{j}(\vec{r}) = \int \Lambda(\vec{r} - \vec{r}')\vec{\nabla}\mu(\vec{r}')d\vec{r}' \qquad [1.10]$$

$\Lambda(\vec{r})$ being the *Onsager coefficient* that will be discussed below. Let us assume an exponential decrease of the fluctuation, as a function of the wave-vector, $\vec{q}$:

$$\delta\Phi(\vec{q},t) = \delta\Phi(\vec{q},0)e^{-t/\tau(q)} \qquad [1.11]$$

Here, $\tau(q)$ is the relaxation rate. Using relations [1.9] to [1.11] and keeping only the linear terms in the fluctuation of composition, the following result is found (Cahn 1968):

$$\tau^{-1}(q) = -\frac{1}{\delta\Phi_q}\frac{\partial(\delta\Phi_q)}{\partial t} = q^2\Lambda(q)\left[(\chi_c - \chi) + q^2 + \frac{C}{q^2}\right] \qquad [1.12]$$

Equation [1.12] then provides the relaxation rates for the first instants, when the linearization procedure is valid. Positive relaxation rates correspond to stable cases when fluctuation decreases in time, while negative rates correspond to unstable modes. Such fluctuations increase in time (Binder and Heermann 1985). In order to determine the relaxation rate, we need to know Onsager transport coefficients, $\Lambda(q)$, and therefore the nature of the strand motion. The shape of equation [1.12] indicates that the product of the last two terms is a diffusion-coefficient. As usual, this coefficient is the ratio of mobility, μ, to the correlation function, that is:

$$D(q) = \mu(q) / S(q) \qquad [1.13]$$

Comparing it with relation [1.6], we find that the Onsager coefficient can be interpreted as the mobility of strands. In a highly cross-linked system, such as

considered here, the motion of polymer-chains is local, over a distance $d \cong n^{1/2}a$, where a is the common size of monomers and n is the number of monomers between consecutive cross-links (polymerization-degree of strands). Notice that, for highly cross-linked polymer blends, with $n < N_e$, where N_e is the distance between consecutive entanglements, only Rouse motion is present. Onsager transport coefficient, $\Lambda(q)$, is then proportional to Rouse mobility. It is emphasized that the case with $n >> N_e$ is discussed in section 1.4 (see below). For high cross-linked blends, the number $n(q)$ of monomers in a strand at distance q^{-1} is proportional to q^{-2}. Within the framework of Rouse approximation, the mobility is as follows:

$$\Lambda(q) \cong n^{-1}(q) \cong (qa)^2 \qquad [1.14]$$

Then, we have:

$$\tau^{-1}(q) = q^4\left[(\chi_c - \chi) + q^2 + \frac{C}{q^2}\right] \qquad [1.15]$$

Figure 1.1 shows the characteristic frequency, for various cases, $\Omega_1(q) = \tau^{-1}(q) / q^4$. Figure 1.1(a) describes the case in the absence of cross-links and for the first instants of dynamics. For $\chi < \chi_c$ (or $T > T_c$), all frequencies are positive and therefore there is no instability. In the opposite case, $T < T_c$, however, we find that all modes with:

$$q > q_c \cong (\chi - \chi_c)^{1/2} \qquad [1.16]$$

are stable, while the long wavelength modes with $q < q_c$ are unstable. Any fluctuation with such a wavelength increases in time. For a cross-linked polymer blend, for which the rigidity constant, C, is non-zero, the situation is quite different (Figure 1.1(b)). For $\chi < \chi_c$, the curves have a minimum that can be either positive or negative. For $\chi < \chi_s$, all frequencies are positive, and then, there is no instability. Let us recall that:

$$\chi_s - \chi_c \cong C^{1/2} \qquad [1.17]$$

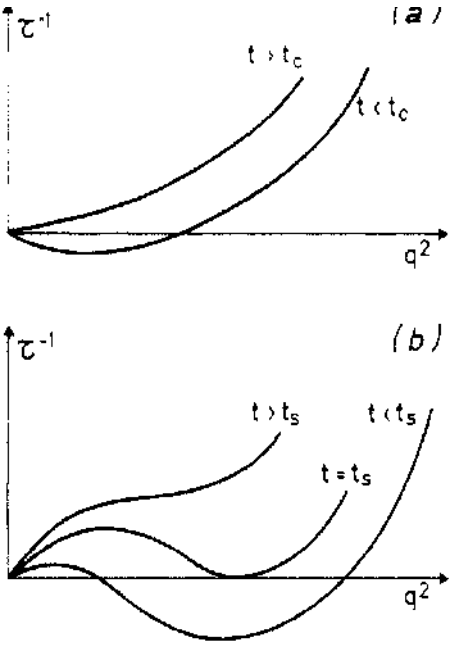

Figure 1.1. *(a) Relaxation rate, as a function of the wave number, for a non-cross-linked blend. For* $\chi > \chi_c$ *, the small* q *modes are unstable. (b) Relaxation rate for a cross-linked blend. For* $\chi_c > \chi > \chi_s$ *, the minimum is positive and then there is no instability. Above* χ_s *, the minimum becomes negative and the modes are unstable for a large* q

For $\chi = \chi_s$, the minimum of the characteristic frequency becomes *zero*, and the latter corresponds to a microphase separation. For low temperatures, $\Omega_1(q)$ has a negative part corresponding to the presence of instabilities in a finite interval of wave-vector, q. The most fast increasing instability corresponds to the minimum of the curve for:

$$q_{\min}^2 \cong \chi - \chi_c + \left[(\chi - \chi_c)^2 - 3C \right]^{1/2} \qquad [1.18]$$

The condition, $\chi \cong \chi_s$, corresponds to the size, q^{*-1}, of microdomains. As shown above, this can be written under the following scale form:

$$q^2 = (\chi_c - \chi) f\left(C / (\chi_c - \chi)^2 \right) \qquad [1.19]$$

It is important to note that the fact that the short wavelength part, q, of the curves is canceled out is a consequence of the scattered intensity, $S(q)$, which vanishes at $q = 0$. This is in perfect agreement with the results of the neutron scattering experiment realized by Briber and Bauer. Therefore, the previous considerations should not be expected to be valid in this region. This question will be reexamined in the next section. Finally, near typical size, q^{*-1}, the characteristic frequency varies as follows:

$$\Omega\left(q^{*}\right) \cong q^{*4}\left(\chi_s - \chi\right) \qquad [1.20]$$

with:

$$\chi_s = \chi_c + q^{*2} \qquad [1.21]$$

This characteristic frequency vanishes when χ is close to its spinodal value, χ_s. Therefore, the modes are slower than those of Rouse. It is important to note that according to relation [1.15], for $\chi = \chi_c$, the characteristic frequencies vary as follows:

$$\Omega\left(q\right) \cong q^{6} \qquad [1.22]$$

Similar results have been previously found for a common polymer blend and have been interpreted as a weighted average of two characteristic rates, namely, local motions of Rouse type and long chain reptation.

The remaining part corresponds to a slow decrease related to the presence of spinodal decomposition.

1.4. Discussion

The previous sections discussed kinetics over short periods of time of microphase separation occurring in blends made of two chemically incompatible polymers, cross-linked in the single-phase region and brought to the demixing region by a progressive temperature decrease. According to our predictions, only a local motion of Rouse type is possible, due to the presence of permanent cross-links. This same motion occurs inside microphase domains. As a result, we found that the characteristic rate varies with the wave-vector as q^{6} at spinodal temperature.

Furthermore, in the single-phase region, instabilities increase with a characteristic time, $\Omega_q \cong q^4(\chi_s - \chi)$, where χ is the segregation parameter, which varies essentially as the inverse of the absolute temperature, and χ_s is its spinodal value.

For the present study, the approximation made is that there is only one temperature in the problem. More precisely, crosslinking of the random blend of species is produced at high temperature, far away from the critical point. It is important to note that the above-mentioned theory of microphase separation shows that the theoretical scattering intensity vanishes when the scattering angle is zero. However, Briber and Bauer have experimentally shown that this is not the case. This discrepancy between theory and experiment has been explained by a series of published works (Vilgis et al. 1993; Benmouna et al. 1994b; Bettachy et al. 1995). In fact, the origin of this discrepancy is the existence of initial composition fluctuations at the moment of blend crosslinking. These fluctuations exist even at very high temperature.

It is important to note that the above considerations can be extended to the case of weakly cross-linked polymer gels, and let us extend kinetics study to these gels. For long polymer chains, the number of monomers between consecutive cross-links, n, is larger than the number of entanglements, N_e, and in this case, kinetics results from a reptation inside tubes between crosslinking points, over long periods of time. In this case, Onsager coefficient, $\Lambda(q)$, no longer corresponds to the local motion of Rouse type, but to a local reptation motion of strands inside tubes. According to Pincus (1981), such a motion implies:

$$\Lambda(q) \cong (qn)^{-2} \qquad [1.23]$$

and therefore:

$$\tau^{-1}(q) \cong n^{-2}\left[(\chi_c - \chi) + q^2 + \frac{C}{q^2}\right] \qquad [1.24]$$

There is a change in behavior between relations [1.15] and [1.24] for $n \cong N_e$. According to relation [1.24], there is a fast instability for $q \cong q^*$, for which the characteristic frequency increases as follows:

$$\tau^{-1}(q^*) \cong n^{-2}(\chi_s - \chi) \qquad [1.25]$$

It is important to note that when the rigidity constant of gel, C, tends to zero, the previous relation becomes quantitatively similar to that of Pincus relative to a non-cross-linked polymer blend undergoing a macrophase separation:

$$\tau^{-1}\left(q^{*}\right) \cong N^{-2}\left(\chi_c - \chi\right) \cong N^{-2}t \qquad [1.26]$$

With the deviation from the critical temperature:

$$t = \left(\chi_c - \chi\right) / \chi_c \qquad [1.27]$$

This chapter, whose content is largely based on a previously published work (Battachy et al. 1992), focused on interpenetrating gels in a molten state. However, the extension of the present study has been achieved for interpenetrating gels in the presence of a solvent (Vilgis et al. 1993; Benmouna et al. 1994b; Bettachy et al. 1995; Benhamou et al. 1997; Derouiche et al. 2005; Benhamou et al. 2010). In this case, crosslinking was achieved at high temperature, therefore, under good solvent conditions. The essential change is that kinetics is this time governed by a local motion of Zimm type (Derouiche et al. 2005), where strands are subjected to hydrodynamic interactions.

Finally, it should be recalled that this study has been extended to the case of interpenetrating gels formed by a crosslinking of polyelectrolyte-chains (Benmouna et al. 1994a; Boussaid et al. 2009), and it has been shown that the sign of charges along chains and the ionic concentration of co-ions and counter-ions induce radical changes in kinetics of the microphase separation.

1.5. References

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