Phase-Boundaries near Critical End points: Applications to Cross-linked Copolymers

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Abstract

The phase behavior of a cross-linked polymer blend made of two incompatible species, $A$ and $B$, of different chemical nature is analyzed. Besides a homogeneous phase, this system also exhibits two microphases and a phase of total segregation. The transition between the homogeneous and the microphase is continuous along a $\lambda$-line; a first-order phase boundaries separate the microphase and the disordered phase from the phase of complete segregation. The critical line meets the first-order phase boundaries at an end point. Scaling arguments indicate that, close to any end point, the equations for the first-order phase boundaries exhibit nonanalyticities associated with the singularities present at the thermodynamic functions near the critical line. Explicit expressions for the phase boundaries near the end point for a cross-linked polymer mixture are obtained and checked for singularities.

1 Introduction

Polymer mixtures were usually phase separated. When the chains are long, the translational entropy of the chain is small and any chemical difference between the two species leads to a repulsion and consequent phase separation at a temperature $T = T_0$. One way to prevent phase-separation is to cross-link the system at high temperatures and then brought it to the co-existence region. A competition between the natural tendency of the system
to phase separate and the elastic forces due to the presence of the cross-
links is established. As a result of this competition, there is a microphase
separation. For strongly cross-linked system, the distance between two
cross-links is fixed and the cross-links are permanent. In this case, the mi-
crophase separation happens at a temperature lower than the temperature
for which complete segregation would had occurs $T_m < T_0$.

When the number of cross-links is not too large, the distance between
cross-links it is not fixed and the position of each $A$-$B$ link fluctuates in
space. Then, as these inhomogeneities in the links are to be taken taken into
account, the phase-diagram of the system changes quite drastically.

Besides the homogeneous phase and the microphase, one also finds a phase
of complete segregation. This phase is separated from the homogeneous and
microphase by first-order phase boundaries. The critical line between the
disordered and the microphase meets these phase boundaries at an end point
where the three phases coexist.

It is well known that in the vicinity of continuous transitions, singular-
larities in the thermodynamic functions such as compressibility, specific heat
and density should be expected. These nonanalyticities are usually expressed
through universal critical exponents and universal amplitude ratios that one
can measure. However, some time ago, it was shown, through a phe-
nomenological argument, that in the vicinity of an end point, singularities
in the first order phase boundaries should also be expected and that these
singularities could also be expressed in terms of universal exponents and uni-
versal amplitude ratios. Nevertheless, this assumption is based on scaling
arguments and needs to be checked. This was already done in the spherical
model. Unfortunately the spherical model has no physical realization and,
consequently, we indeed need to check our theory in an more realistic model.

In this sense, our aim in this paper is to show that these singularities
are actually present in the first-order phase boundaries of the polymer mix-
ture described above. In order to do so, on basis of an effective mean-field
theory that takes into account anisotropy between the two species and in-
homogeneities in the cross-links, we calculate the phase boundaries near the
end point. The remainder of this paper is organized as follows. In sec. 2, we
briefly review the scaling arguments that led us to the conclusion that near
the end points singularities in the phase boundaries might exist. Accepting
the plausibility but the uncertainty of this conclusion, in sec. 3, we test them
in a model for polymer mixture. Our results are summarized in sec. 4.
2 Phase Boundaries near Critical End points

Before analyzing the phase-diagram of the copolymers, it would be helpful to review the theory for singularities in the phase boundaries near end points \[6\]-\[9\]. In the space \((T,g,h)\) (here \(g\) is an intensive parameter that can be a pressure, external field, chemical potential, etc), an end point is the locus where two phases, \(II^+\) and \(II^-\), become critical in the presence of a third noncritical phase, \(III\) (see Fig.1). Now, what is the form of the phase boundary \(g_\rho(T,h)\) that separates the critical phases from the spectator phase when \((T,h)\) pass through \((T_e,h=0)\)? At the end point \(g\) has a definite value, \(g_e\), and so do the slopes \(g_1 \equiv dg_\rho/dT \mid e\) and \(g_2 \equiv dg_\rho/dh \mid e\). Thus, it seems likely that most people would assume that

\[
g_\rho = g_e + g_1 t + g_2 h + \ldots \text{ and further analytic terms} \quad \text{in the Taylor series expansion in powers of} \quad t = (T - T_e)/T_e \quad \text{and} \quad h. \quad \text{However, this is wrong. Fisher and Barbosa (FB) [6] have shown that} \]

the full expression for \(g_\rho\) given by

\[
g_\rho = g_e + g_1 t + g_2 h - X_\pm |t|^{2-a} - Y |t|^\beta |h| - Z_\pm |t|^{-\gamma} h^2 + \ldots \quad (1)
\]

contains nonanalyticities related with the singularities at the critical line. Here + means the disordered phase \((I)\) and the − refers to the ordered phases \((II^\pm)\), the exponents \(\alpha, \beta\) and \(\gamma\) are the specific heat, the order parameter and the susceptibility critical exponents associated with \(\lambda\) line. Similarly the amplitudes \(X_\pm, Y\) and \(Z_\pm\) are universally related to the critical amplitudes by

\[
\begin{align*}
\frac{X_+}{X_-} &= \frac{A_+}{A_-} \\
\frac{Z_+}{Z_-} &= \frac{C_+}{C_-} \\
\frac{X_+Z_+}{Y^2} &= \frac{A_+C_+}{(2-\alpha)(1-\alpha)B^2}
\end{align*}
\]

where \(A_\pm, B\) and \(C_\pm\) are the critical amplitudes for the specific heat, for the order parameter and for the susceptibility near the critical line respectively.

But this is not the only nonanalyticities present in this phase boundary. Indeed the intersection of the surface \(\rho\) with the plane \(t = 0\) is a curve that near the end point can be written as

\[
g_c(h) = g_e - Y_c |h|^{1+1/\delta} \quad (3)
\]
where $\delta = \beta \Delta$ and where $\Delta$ is the gap exponent of the critical region. Here, as before, the coefficient $Y_c$ is also related to the critical amplitudes by

$$\frac{Y^{\delta-1}Z_+}{Y^\delta_c} = \left(\frac{\delta + 1}{\delta}\right)^{\delta} \frac{B^{\delta-1}A_+}{B^\delta_c}. \quad (4)$$

Therefore, if the $\lambda$-line would be classical, FB’s theory predicts that the phase boundary $g_\rho$ given by Eq. (4) would have two nonanalytic terms with exponents $\beta = 1/2$ and $\gamma = 1$, while the phase boundary $g_c$ given by Eq. (3) would have one singular term with exponent $\delta = 3$. These are the usual mean-field critical exponents. Besides, FB approach also predicts that the coefficients $Z_\pm$, $Y$ and $Y_c$ would be universally related to the critical amplitudes $C_\pm$, $B$ and $B_c$ by

$$\frac{Z_+}{Z_-} = \frac{C_+}{C_-} = 2 \quad (5)$$

$$\frac{Y^{\delta-1}Z_+}{Y^\delta_c} = \left(\frac{\delta + 1}{\delta}\right)^{\delta} \frac{B^{\delta-1}A_+}{B^\delta_c} = \left(\frac{4}{3}\right)^3.$$  

### 3 Phase-Diagram of Crossliked Copolymers

In this section, we investigate the melt of a non compatible and cross-linked mixture of polymers $A$ and $B$ using the Landau-Ginzburg-Wilson-de Gennes’ Hamiltonian

$$\beta H = \int d^3r \left\{ \frac{(a \nabla \phi(r))^2}{48} + \frac{\tau}{2} \phi(r)^2 + u \phi(r)^4 - h(r) \phi(r) + \frac{C(r)P(r)^2}{2} \right\} \quad (6)$$

where $a$ is the size of one monomer and where the order parameter $\phi(r)$ is given in terms of the local fluctuations of the density of each specie, $\phi_A(r)$ and $\phi_B(r)$ by

$$\phi_A(r) = \frac{1}{2} (1 + l(r) + \phi(r))$$

$$\phi_B(r) = \frac{1}{2} (1 - l(r) - \phi(r)). \quad (7)$$

Here $\langle \phi_A(r) \rangle = 1/2(1 + \langle l(r) \rangle)$ and $\langle \phi_B(r) \rangle = 1/2(1 - \langle l(r) \rangle)$ are the volume fractions of each type of polymer. A nonzero value of $\langle l(r) \rangle$ allows for different
volume fractions of each specie. The term linear in $\phi(r)$ in Eq. (9) contains the difference in the chemical potential between the two types of polymer. In each cross-link, two monomers one belonging to the specie $A$ and another to the specie $B$ are tied together. However they can be displaced slightly, leading to an elastic "polarization" given by

$$\vec{P} = \frac{1}{V} (\sum_{i \in A} \vec{r}_i - \sum_{j \in B} \vec{r}_j)$$

where $\vec{r}_i$ is the position of the $i$ monomer at a polymer of type $A$ while $\vec{r}_j$ is the position of the $j$ monomer of type $B$ and where $V$ is the total volume of the system. In the same way that for the electrostatic case, polarization and charge are not independent quantities, here the elasticity and the volume fraction of each specie are also related by $\nabla \cdot \vec{P} = \phi(r) + l(r)$.

Consequently, the last term at the Hamiltonian Eq. (6) contains the elastic contribution associated with the cross-links. For simplicity, we assume that this term has a quadratic form that resembles the energy of a spring system. $C(r)$ is the internal rigidity is given by $C(r) = C_0 \sum \delta(\vec{r} - \vec{r}_i)$ where here $\{\vec{r}_i\}$ correspond to coordinates of $N_c$ cross-links distributed in the volume $V$ according a Poisson distribution characterized by $\langle C(r_1)C(r_2) \rangle = C_0 \langle C(r_1) \rangle \delta(r_1 - r_2)$.

Since the cross-links are not permanent, they can open and close. Consequently the disorder is assumed to be annealed. Then, the resulting effective hamiltonian obtained after averaging over this distribution is given by

$$\beta H_{eff} = \int d^3r \{ a^2 \frac{(\nabla \phi(r))^2}{48} + \frac{\tau}{2} \phi(r)^2 + u \phi(r)^4 - h(r) \phi(r) \} + \frac{1}{n} \int d^3r [1 - e^{-C_0 P^2/2}].$$

where $n = V/N_c$ (actually $1/n$ is the density of cross-links). If the gel is very dense, $n$ will be related to the average number of monomers between two cross-links.

Now, one has to eliminate $\vec{P}$ in favor of $\phi(r)$, using the constraint $\nabla \cdot \vec{P} = \phi(r) + l(r)$. Then, the expression for the free energy $\beta F_{eff} = -\ln e^{-\beta H_{eff}}$ can be evaluated at the mean-field level by taking the saddle point approximation, what leads to

$$\beta F_{eff} = \frac{1}{2} \left[ \tau + \frac{(q.e)^2}{24} \right] \psi_q \psi_{-q} + u \psi_q^2 \psi_{-q}^2 - h_{-q} \psi_q + \frac{1}{n} \left[ 1 - e^{-C_0 P^2/2} \right].$$
where the expressions for $\psi_q$ and $q_c$ are given by the equations

$$
\frac{\partial \beta H_{\text{eff}}}{\partial \phi(q)} \bigg|_{\phi_q=\psi_q, q=q_c} = \left[ \tau + \frac{(q_c a)^2}{24} \right] \psi_{-q_c} + 4u\psi_{-q_c}^2 \psi_{q_c} - h_{-q_c}
$$

and

$$
\frac{\partial \beta H_{\text{eff}}}{\partial q} \bigg|_{\phi_q=\psi_q, q=q_c} = \frac{a^2 q_c}{24} \psi_{q_c} \psi_{-q_c} - \frac{c}{q_c^2} \psi_{-q_c} e^{-cn\psi_{q_c}\psi_{-q_c}/(2q_c^2)}
$$

and where $c = C_0/n$. From the above equations we can see that the system exhibits four possible phases:

(a) phase $I$, a homogeneous phase where $\psi_I \to 0$ as $h_{q_I} \to 0$ and where $q_c = q_I \neq 0$;

(b) phases $II_+$ and $II_-$, two microphases where partial segregation occurs, where $\psi_{II} \not\to 0$ as $h_{q_{II}} \to 0$ and where $q_c = q_{II} \neq 0$.

(c) phase $III$, a complete segregated phase, where $\psi_{III} \not\to 0$ as $h_{q_c} \to 0$ and where $q_c = q_{III} = 0$.

The free energy associated with each one of these phases is given by

$$
\beta F_I = \frac{1}{2} \left[ \tau + \frac{(aq_I)^2}{24} \right] \psi_{I}^2 + u\psi_{I}^4 + \frac{1}{n} \left[ 1 - e^{-cn\psi_{I}^2/(2q_I)} \right] - h_{-q_I}\psi_I
$$

for the phase $I$,

$$
\beta F_{II} = \frac{1}{2} \left[ \tau + \frac{(aq_{II})^2}{24} \right] \psi_{II}^2 + u\psi_{II}^4 + \frac{1}{n} \left[ 1 - e^{-cn\psi_{II}^2/(2q_{II})} \right] - h_{-q_{II}}\psi_{II}
$$

for phase $II$ and

$$
\beta F_{III} = \frac{\tau}{2} \psi_{III}^2 + \frac{u}{4} \psi_{III}^4 + \frac{1}{n}
$$

for the phase $III$. Here the values of $\psi_I, \psi_{II}, \psi_{III}, q_I$ and $q_{II}$ are given by the saddle point solutions of Eq. (11) and Eq. (12).
By comparing the above free energies we find the phase-diagram illustrated in fig. 2 that goes as follows [5]. At high values of $\tau$ that here plays the role of temperature, the two species are mixed at phase $I$. For strongly cross-linked system, low values of $n$, as the temperature is decreased, one finds at $\tau = \tau_e$ a continuous phase transition to the microphase (phase $II$). If the temperature is decreased even further, one meets a first-order phase boundary between the microphase, phase $II$, and a state where the two species are completely segregated, phase $III$. When the system is weakly cross-linked, the number of monomers between two cross-links, $n$, is large and consequently, as the temperature is decreased, one finds a first-order phase transition between the homogeneous state, phase $I$, and the state where the segregation is total, phase $III$. The three phases, $I$, $II$ and $III$ meet at the end point $e$ at $(\tau = \tau_e, n = n_e, h = 0)$.

Then, in order to check if our predictions summarized at the Eq. (1), Eq. (3), Eq. (2) and Eq. (4), are correct, we will obtain the expression for the phase boundary $\rho$ near the end point. First, by equating the free energy of the homogeneous phase given by Eq. (13) to the free energy of the phase $III$ given by Eq. (15) we find the expression

$$\tau_{\rho^+} = \tau_e + g_1 (n - n_e) - X_+ \mid n - n_e \mid^{2-\alpha} - \frac{1}{2} Z_+ \mid n - n_e \mid^{-\gamma} h^2$$

for the phase boundary $\rho^+$ near the end point when $n > n_e$. Here the exponents are $\alpha = 0$ and $\gamma = 1$ while the non-universal coefficients are

$$g_1 = \frac{c^{3/2}}{u}$$
$$X_+ = \frac{c^{5/2}}{4u^2}$$
$$Z_+ = \frac{u^2}{c}.\tag{17}$$

Similarly, equating the free energy of the microphase, phase $II$, given by Eq. (14) to the free energy of the phase $III$ given by Eq. (13), we obtain the expression for the phase boundary $\rho^-$ near the end point when $n < n_e$ namely

$$\tau_{\rho^-} = \tau_e + g_1 (n - n_e) - X_- \mid n - n_e \mid^{2-\alpha} - Y \mid n - n_e \mid^{\beta} h \mid$$
$$- Z_- \mid n - n_e \mid^{-\gamma} h^2$$

$$\tag{18}$$
where $\alpha = 0$, $\beta = 1/2$ and $\gamma = 1$, where the coefficient $g_1$ is the same as the one obtained in Eq. (17) as we have predicted (see Eq. (1)) and where

$$
X_- = \frac{5c^{5/2}}{4u^2} \tag{19}
$$

$$
Y = \sqrt{2c^{1/4}}
$$

$$
Z_- = \frac{u^2}{2c^2}.
$$

Now, one can easily verify that the ratios Eq. (2) built on basis of Eq. (17) and Eq. (19) are universal and given by the values predicted at Eq. (5).

The intersection of the plane $n = n_e$ with the surface $\rho$ is a curve given by

$$
\tau_c(h) = \tau_e - Y_e |h|^{1+1/\delta} \tag{20}
$$

where $\delta = 3$ as we have predicted and where

$$
Y_e = \frac{4(2u^2)^{1/3}}{3c^{1/2}}. \tag{21}
$$

Using the value above for the coefficient $Y_e$ together with Eq. (17) and Eq. (19) we obtain the universal values predicted by Eq. (5).

### 4 Results and Conclusions

Scaling arguments indicate that near any critical end point the phase boundaries must exhibit a nonanalyticities related to the singularities of the critical line.

In order to verify if this prediction based in a phenomenological approach is actually correct, we have looked for a realistic system that exhibits an end point. Therefore, we have studied the phase behavior of a mixture of two incompatible polymer species, $A$ and $B$, that at high temperatures are cross-linked. The phase-diagram for an asymmetric polymer blend with inhomogeneities in the cross-links, illustrated in figure 2, exhibits a critical end point where the four phases present in this system, a homogeneous phase, two microphases and a phase of complete segregation, meet. Then, using a
mean-field theory, expressions for the phase boundaries separating the critical phases from the non-critical phase were derived. Finally we checked that these equations exhibit nonanalyticities associated with the mean-field critical exponents of the specific heat, \( \alpha = 0 \), of the order parameter \( \beta = 1/2 \), of the isothermal compressibility, \( \gamma = 1 \) and of the order parameter at the critical temperature \( \delta = 3 \). We also verified that the coefficients \( X_\pm, Z_\pm, Y \) and \( Y_c \) are universally related to the critical amplitudes \( A_\pm, C_\pm, B \) and \( B_c \) as was predicted in Eq. (2) and in Eq.(4). The universal ratios assume the classical values given by Eq. (3).

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FIGURE CAPTION

Figure 1. Schematic phase-diagram $t \times g \times h$. The phase $I$ is the disordered phase, phase $II_{\pm}$ are the two ordered phases and phase $III$ is the noncritical phase. The line $\lambda$, dashed line, is a continuous transition, the planes $\rho$ and $\eta$ are first-order phase boundaries and $e$ locates the end point. The first-order lines $\sigma_{\pm}$ are the intersection of the surface $\rho$ with the plane $h = 0$.

Figure 2. Phase-diagram $n \times \tau \times h$ for a $A-B$ polymer bend. The phase $I$ is the homogeneous phase, phases $II_{\pm}$ are the microphases and phase $III$ is the phase where the segregation is total. The line $\lambda$, dashed line, is a continuous transition, the planes $\rho$ and $\eta$ are first-order phase boundaries and $e$ locates the end point. The first-order lines $\sigma_{\pm}$ are the intersection of the surface $\rho$ with the plane $h = 0$. 