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Coarsening Dynamics in Cross-Linked Polymers

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Abstract. — We study the dynamics of a pure-phase domain in a quenched melt of cross-linked polymers. Starting from de Gennes's mean-field theory, we obtain a pinning down of the coarsening process at a characteristic scale, which depends both on the rigidity constant and on the depth of the quench. Relaxation to the microdomains exhibits a critical slowing down in a whole range of parameters: this reduces the stability region of the modulated phase.

1. Introduction

After the pioneering paper by de Gennes [1] various experimental and theoretical studies have been dedicated to phase separation in binary polymer blends in the presence of cross-links.

That static analysis was confirmed by Briber and Bauber [2] in an experiment where various types of cross-links (A–A, A–B and B–B) were produced with γ-rays over a blend of deuterated polystyrene and poly(vinyl methyl ether).

Recent results deal with the dynamics of phase separation in systems where only one of the two components undergoes a cross-linking process. Aqueous solutions of dextran and gelatin have been studied by time-resolved light scattering [3]. In that work, above the gelation temperature, phase separation dominated by hydrodynamics was observed (the domain size $R$ growing as $R(t) \sim t^z$ with $z \equiv 1$). Below the gelation temperature smaller values of $z$ ($z \approx 0.4, 0.3$) were obtained and, further below, values even smaller than $\frac{1}{2}$: this was interpreted as a precursor of the complete pinning down of the structure. In another experiment, polyacrylamide gels grown in the presence of varying amounts of polyethyleneglycol (PEG) have been studied [4]. Both gelation and polymerization were photoinduced. Again, microsegregation was obtained; as a matter of fact in such systems pores of sizes up to two orders of magnitude above the usual nanometers can be generated by varying the PEG concentration.

In a different context, dilute silica gels imbied with a mixture of water and isobutyric acid were pressure-quenched into the pure-phase coexistence region, and a coarsening consistent with a diffusion-driven phase separation ($z = \frac{1}{3}$) was observed, with no evidence of domain

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pinning [5]. We notice that in this system there is no competition between gelation and phase separation, but rather phase separation in a porous medium.

On the theoretical side, the original de Gennes’s model has been modified to include screening effects generated by fluctuations in the concentration of cross-links (Refs. [6] and [7]). Further work [8] refers to the case in which cross-links are produced during phase separation: it is shown that the spinodal instability may still occur in an “opaque” gel. The static analysis of the system at criticality has been accomplished by means of renormalization group by Benhamou [9].

In this paper, our aim is to study the dynamics of a single-phase domain, after quenching in the coexistence region, when long range elastic interactions mimic the effect of the cross-links. The analysis is based on de Gennes’s theory, so that, strictly speaking, our results should be compared with a dynamic version of the experiment described in reference [2].

It has been very recently shown [12] by the replica method that the Deam-Edwards Hamiltonian including cross-links allows for a mean-field solution which exactly coincides with the original de Gennes free energy, apart from a renormalization of the elastic constant. As long as we consider deep quenchings we can neglect fluctuations, which are relevant close to the critical point.

2. Time-Independent Ground State

We start with the Flory-Huggins description of the mixture of two polymeric species, say A and B, with polymerization degrees $N_A$ and $N_B$ respectively [13]. The free energy in terms of the volume fraction $\varphi$ of species A is given by

$$\frac{F_{\text{mix}}}{K_B T} = \frac{1}{N_A} \varphi \ln \varphi + \frac{1}{N_B} (1 - \varphi) \ln (1 - \varphi) + \chi \varphi (1 - \varphi),$$

(1)

where $\chi$ is the Flory interaction parameter.

As suggested by de Gennes [1], the effect of cross-links between monomers of different species can be described by means of an electrostatic analogy, where the two species carry opposite unit charges per monomer and the melt acts as a dielectric material. This leads to a polarization $\mathbf{P}$, contributing to the free energy with a term

$$\frac{F_{\mathbf{P}}}{K_B T} = \frac{1}{2} C \mathbf{P^2}$$

(2)

$$\nabla \cdot \mathbf{P}(r) = -\rho(r).$$

The rigidity constant $C$ has been estimated [1] to be of the order $\frac{1}{n^2 a^2}$, $n$ being the average number of monomers between adjacent cross-links and $a$ the size of the monomer (this behavior, apart from the coefficient, has been confirmed in [12]). Here we assume the material to be globally neutral; $\rho(r)$ describes the local deviation from the average volume fraction $\frac{1}{2}$ ($\varphi(r) = \frac{1}{2} + \frac{1}{2} \rho(r)$).

The total free energy is then

$$\frac{\mathcal{F}[\varphi]}{K_B T} = \int \frac{F}{K_B T}$$

(3)

$$\frac{F}{K_B T} = \frac{F_{\text{mix}}}{K_B T} + \frac{F_{\mathbf{P}}}{K_B T} + \frac{1}{2} A |\nabla \varphi|^2$$

(4)

where $A$ is an elastic constant ($A \sim a^2$). Upon expanding up to the quadratic order in $\rho$ we obtain

$$\frac{\mathcal{F}[\rho]}{K_B T} = \int \frac{f_0 + h \rho + \frac{1}{2} t \rho^2 + \frac{1}{2} C \mathbf{P^2} + \frac{1}{2} A |\nabla \rho|^2 + O(\rho^3)}{K_B T}$$

(5)
where \( f_0 \) and \( h \) depend on \( N_A, N_B \), \( t = \frac{1}{2}(\chi_c - \chi) \), \( \chi_c \) corresponding to volume fraction \( \frac{1}{2} \). Note that if \( N_A = N_B \) one has \( h = 0 \) and \( \mathcal{O}(\rho^4) \) is replaced by \( \mathcal{O}(\rho^2) \).

The Green’s function exhibits a peak at a wave vector \( q_C = (\frac{\gamma}{\mathcal{C}})^{\frac{1}{4}} \sim \frac{1}{\sqrt{n\alpha}} \); this is interpreted as a modulation of the melt in microdomains (notice that no interface energy is taken into account). This modulation is present, in the \((C,t)\) plane, in the region above the branch of parabola \( t = -2A^\frac{1}{3}C^\frac{2}{3} \). This mean-field result is modified by renormalization group into \( -t \sim C^\frac{1}{3} \), where \( \phi \cong 2.5 \) in three dimensions [9].

Our aim is to examine the time evolution of monophasic domains when the system is forced at the boundary by a flux of material.

In terms of the chemical potential \( \mu = \frac{\delta F[\rho]}{\delta \rho} \),

\[
\mu = h + t\rho - A\Delta \rho - C\Delta^{-1} \rho,
\]

the current is \( \mathbf{j} = -M \nabla \mu \).

Here and in the sequel we assume the mobility \( M \) to be independent on concentration and on lengthscale. It is known that in general the mobility of polymers actually depends on lengthscale [10]. We exclude the case of strong gels, arising when \( n \ll N_E \), \( N_E \) being the average number of monomers between entanglements: the kinetics of this case, characterized by a Rouse behavior \( M \sim q^2 \), has been analyzed in [11]. As illustrated by Pincus [10], at intermediate times, one has \( M \sim q^{-2} \left( 1 - \exp \left( -\frac{q^2 R_0^2}{6} \right) \right) \), \( R_0 \) being the unperturbed Gaussian chain radius. After saturation, when \( qR_0 \ll 1 \), \( M \) goes to a constant and phase separation proceeds by droplet growth trough accretion: our model refers to these late stages of the coarsening.

The thermodynamic equation of motion, sometimes called the Cahn-Hilliard equation, has then the following form

\[
\frac{\partial \rho}{\partial \tau} = M\Delta \left( \frac{\delta F[\rho]}{\delta \rho} \right). \tag{6}
\]

Notice that if one removes the assumption of global neutrality, one is left with a divergent additive constant in the chemical potential. This has no effect on the dynamical equation (6): hence our treatment is valid for the general case.

We first determine the time independent spherically symmetric solutions of equation (6) satisfying:

\[
[\Delta^2 - t_A \Delta + C_A]\rho_s(r) = 0 \tag{7}
\]

where \( t_A = \frac{t}{\mathcal{A}} \) and \( C_A = \frac{C}{\mathcal{A}} \).

When \( t_A^2 \leq 4C_A \) they have the form:

\[
\rho_{1s}(r) = \frac{a_1}{r} \left[ \exp \left( -\frac{r}{\xi} \right) \cos \left( \frac{r}{\lambda} + \theta \right) \right], \tag{8}
\]

where \( a_1 \) and \( \theta \) are arbitrary constants; \( \xi \) and \( \lambda \) are dependent on the two scales \( C_A^{-\frac{1}{4}} \) and \( t_A^{-\frac{1}{2}} \) of the free energy and define correlation length and modulation length respectively:

\[
\xi = \frac{2}{\sqrt{2C_A^{\frac{1}{2}} + t_A}}, \quad \lambda = \frac{2}{\sqrt{2C_A^{\frac{1}{2}} - t_A}}. \tag{9}
\]

When \( t_A^2 > 4C_A \) and \( t_A < 0 \), one has instead

\[
\rho_{2s}(r) = \frac{a_2}{r} \left[ \cos \left( \frac{r}{\lambda_1} + \theta_1 \right) + b \cos \left( \frac{r}{\lambda_2} + \theta_2 \right) \right]. \tag{10}
\]
where the lengths $\lambda_1$ and $\lambda_2$ are:

$$
\lambda_1 = \frac{2}{\sqrt{|t_A^2 - 4C_A + t_A|}}, \quad \lambda_2 = \frac{2}{\sqrt{|t_A^2 - 4C_A - t_A|}}.
$$

(11)

The solution (8) is a ground state for the Gaussian theory defined by equation (5), while (10) is not, since it corresponds to a parameter region where the operator (7) is not positive definite.

Notice that at the critical line $t_A = -2C_A^\frac{1}{2}$, where one has: $\lambda = \lambda_1 = \lambda_2 = C_A^{-\frac{1}{4}} = q_c^{-1}$, $\xi \rightarrow \infty$, the two solutions coincide.

Finally consider $t_A^2 > 4C_A$ with $t_A > 0$; in this case the modulated behavior disappears:

$$
\rho_{3s}(r) = \frac{b_1}{r} \exp \left( -\frac{r}{\lambda_1} \right) + \frac{b_2}{r} \exp \left( -\frac{r}{\lambda_2} \right).
$$

The physical meaning of $\xi$ and $\lambda$ is made clear when considering a linear superposition of solutions of type (8), randomly centered in space: one obtains a pattern of coherent domains having size $\xi$, modulated with wavelength $\lambda$. Below the spinodal the correlation diverges and one is left with two modulating lengths $\lambda_1$ and $\lambda_2$.

3. Pure-Phase Dynamics

In order to derive an equation of motion for pure-phase domains, the region of interest is clearly $t_A < 0$, since there, in the absence of cross-links, the two species would be forced to separate.

Fluctuations in the density of cross-links can favor the spontaneous production of monophasic domains. A uniform rigidity coefficient $C$ is clearly meaningful in a mean-field context: in fact, some approaches start with a stochastic function $C$ [14].

By following the procedure described in [15] we look for a solution of equation (6) associated with a spherical bubble of radius $R(\tau)$:

$$
\rho_1(r, \tau) = \frac{a_1}{r} \left[ \exp \left( -\frac{r - R(\tau)}{\xi} \right) \cos \left( \frac{r - R(\tau)}{\lambda} \right) \right]
$$

(12)

for $r \geq R(\tau)$.

Similarly, in the unstable region $t_A^2 > 4C_A$, we let

$$
\rho_2(r, \tau) = \frac{a_2}{r} \cos \left( \frac{r - R(\tau)}{\lambda_1} \right)
$$

(13)

for $r \geq R(\tau)$.

A growing bubble of B species will have $\varphi = c_\beta$ ($r < R$) and boundary conditions:

$$
\varphi = \begin{cases} 
  c_\alpha + \delta c_\alpha & \text{if } r = R \\
  c_\alpha + \delta c_\infty & \text{if } r \rightarrow \infty.
\end{cases}
$$

Here $c_\alpha$ and $c_\beta$ are the equilibrium volume fractions in the absence of cross-links and $\delta c_\alpha$ is the excess of A-phase at the boundary of the bubble. This excess can be written in the convenient form

$$
\delta c_\alpha = \frac{2d_0}{R} \Delta c,
$$

(14)
where the capillarity length $d_0$, in terms of the surface tension $\sigma$ and the susceptibility $\tilde{\chi}$, has the form [16]:

$$d_0 = \frac{\sigma \tilde{\chi}}{(\Delta c)^2}.$$

Notice that $\delta c_\infty$ corresponds to a forcing term. As we will show, this choice of boundary conditions allows us to recover the standard Lifshitz-Slyozov result [17] in a suitable limit $C \to 0$.

Upon integrating both sides of equation (6) over a shell $R - \varepsilon < r < R + \varepsilon$ and assuming the internal current to be zero, one obtains

$$\dot{R} = \frac{M}{2(\Delta c - \delta c_\infty)} \left( \frac{\partial \mu}{\partial r} \right)_{r=R+\varepsilon},$$

so that, evaluating $\mu$ by means of (12) (or (13)), one finally determines the equation for $\dot{R}$ in the two regions $t_A^2 \leq 4C_A$ (I) and $t_A < 0$, $t_A^2 > 4C_A$ (II).

We define:

$$R^* = \frac{|t_A|}{2C_A^2}, \quad R_{cr}(\tau) = \frac{2d_0\Delta c}{\delta c_\infty(\tau)}, \quad \lambda^2 = \frac{3d_0|t_A|}{C_A}, \quad D = \frac{MA}{2d_0|t_A|};$$

notice that $D$ has the dimensions of a volume per time.

In region I we have:

$$\dot{R} = D \left[ 2 \left( \frac{1}{R_{cr}(\tau)} - \frac{1}{R} \right) \left( \frac{1}{R^*} - \frac{1}{R} \right) - \frac{R}{R^*} \right]$$

where the minus sign corresponds to $t_A < 0$ and the plus sign to $t_A > 0$.

In region II:

$$\dot{R} = D \left[ 4 \left( \frac{1}{|t_A|\lambda^2} - \frac{1}{R_{cr}(\tau)} \right) \left( \frac{1}{R} - \frac{1}{R_{cr}(\tau)} \right) - \frac{R}{R^*} \right].$$

The factor $\left(1 - \frac{1}{|t_A|\lambda^2}\right)$ is always positive and tends to 1 as $C_A \to 0$. Upon selecting a solution corresponding to $\lambda_2$, one would have instead $\left(1 - \frac{1}{|t_A|\lambda^2}\right) \to 0$, as $C_A \to 0$.

In spite of being defined in the unstable region, equation (16) is of interest in that it merges with equation (15) along the critical line, where $\left(1 - \frac{1}{|t_A|\lambda^2}\right) = \frac{1}{2}$: it is the analytic continuation of the ground state excitation in the unstable region. The domain surrounding the bubble should be properly described by a nonlinear kink: this could modify the large time behavior of $R(\tau)$. Our results in region II refer then to the initial stages of the spinodal process.

Equations (15) and (16) describe an isolated pure-phase domain. If we neglect the interaction between domains, a polydisperse assembly of $N$ bubbles will evolve under the mass conservation [17]:

$$\Delta(\tau) + \frac{4}{3} \frac{\pi}{V} \sum_{i=1}^{N} R_i^3(\tau) = Q,$$

where $\Delta(\tau) = \frac{\delta c_\infty(\tau)}{\Delta c}$, $V$ is the volume of the sample and $Q$ the total B-charge; if we assume global neutrality $\bar{Q} = \frac{1}{2}$.

One can argue that under global neutrality to neglect the domain-domain interactions is a rather rough approximation. We notice, as already stated, that our treatment actually holds in the general case; similarly one verifies that equation (5) can be derived by the replica trick for a generic charge [12].
4. Stationary State

Let us first consider \( t_A < 0 \) in region I. If one deals with a monodisperse assembly, the equation (17) can be substituted in the evolution equation and the steady state is determined by the zeros of a fifth order polynomial. It turns out that only one of such zeros is real: hence in the monodisperse case the system relaxes to a fixed size \( R_\infty \), independently on the initial conditions. In numerical computations, starting with a polydisperse configuration, we always observed that the assembly reaches the line \( \Delta + N \frac{4}{3} \pi R^3 = \frac{1}{2} \) in the \( (\Delta, R) \) plane (i.e. becomes monodisperse) before reaching steady state. At later times the system evolves towards the unique intersection \( (R_\infty, \Delta_\infty) \) with the line \( R = f(R, \Delta) = 0 \). Obviously from (17) this steady state depends on the system size \( V \) and on the “total charge” \( Q \).

If, at \( \tau = 0 \), the assembly of bubbles satisfies the conditions \( R < R_{cr}(\tau = 0), R^*, l \) one obtains a behavior \( R(\tau) \sim \tau^{\frac{1}{3}} \) as the intermediate scaling. Analogous behavior is derived from equation (16) when \( R < R_{cr}(\tau = 0), l \). For large enough \( \tau \) the system exponentially approaches \( R_\infty \), with a decay time \( \tau_D = \left( \frac{\partial f(R, \Delta(R))}{\partial R} |_{R=R_\infty} \right)^{-1} \).

Notice that in this region the free energy “mass” coefficient \( t \) is negative. The Lifshitz-Slyozov equation arises as a perturbation of an homogeneous steady state with a positive effective mass coefficient: for this reason the \( R = 0 \) configuration is there always stable. In our case, we perturb an inhomogeneous steady state and \( R = 0 \) is always unstable unless \( t_A > 0 \). The Lifshitz-Slyozov equation can be recovered in our treatment if one lets in the equation (15) \( C_A \to 0 \) with \( t_A \sim C_A^{\frac{1}{2}+\frac{1}{t}} \) and \( 0 \leq \epsilon < \frac{1}{2} \); under these conditions one easily verifies that \( R^*, l \to \infty \).

We now give an estimate of \( R_\infty \) in the limit of low density of cross-links \( (n \gg 1) \), by putting \( C_A = \frac{n}{\alpha^{\frac{3}{2}}} \) and assuming \( \Delta_\infty = 0 \).

In region I with \( t_A < 0 \) we let \( |t_A| = \frac{2\beta_1}{\alpha n^{1+\tau}} (\epsilon \geq 0) \) [18]. We find:

\[
R_{11}^{(l)} \sim \begin{cases} 
\gamma_e \left( \frac{12\beta_1}{\alpha} \right)^{\frac{1}{2}} \left( a^2 d_0 \right)^{\frac{1}{2}} n^{\frac{1}{2}-\frac{1}{t}} & \text{if } 0 \leq \epsilon \leq \frac{1}{4} \\
\sqrt{2} \left( \frac{\beta_1}{\alpha^4} \right)^{\frac{1}{2}} \left( a^n \right)^{\frac{1}{2}-\epsilon} & \text{if } \epsilon > \frac{1}{4}
\end{cases}
\]  

(18)

where \( \gamma_1^\frac{1}{2} = \left( \frac{4}{9} \sqrt{2} \frac{\alpha}{\beta_1} \frac{d_0}{a} + 1 + 1 \right)^{\frac{1}{2}} - \left( \frac{4}{9} \sqrt{2} \frac{\alpha}{\beta_1} \frac{d_0}{a} + 1 - 1 \right)^{\frac{1}{2}} \) and \( \gamma_\epsilon = 1 \) if \( \epsilon \neq \frac{1}{4} \).

Notice that at \( \epsilon = \frac{1}{4} \) the two asymptotic behaviors match continuously as powers of \( n \), with a discontinuity in the coefficient. The result (18) is interpreted as follows: the equilibrium of the bubble in the modulated background must fulfill a stationarity condition of the form

\[
\delta (E_V + E_S + E_B) = 0,
\]

where \( E_V \) and \( E_S \) are the volume and surface energy, while \( E_B = E_B(R) \) is the interaction energy with the background. Although we are not able to give an explicit estimate of \( E_B \), from (18) one concludes that deep inside the region I \( (\epsilon > \frac{1}{4}) \) \( E_B \) and \( E_V \) dominate over \( E_S \), while close to the critical line \( E_B \) becomes comparable with the other terms: this shows up in the \( d_0 \)-dependence of \( R_{11}^{(l)} \).

If one lets \( t_A \) approach zero upon increasing \( \epsilon \) starting from the critical line \( \epsilon = 0 \), the radius of the steady state increases with \( n \) more and more slowly and it tends to zero if \( \epsilon > \frac{1}{2} \).

Notice that the two “natural” lengths \( \lambda \) and \( \xi \) have an asymptotic behavior independent on \( \epsilon \): one has indeed, if \( \epsilon > 0, \lambda \sim \xi \sim (2/\sqrt{\alpha})^{\frac{1}{2}} a\sqrt{n} \).
The decay time \( \tau_D \) in the region \( \epsilon \geq \frac{1}{2} \), in which \( R^{(I)}_\infty \) does not diverge with \( n \), is:

\[
\tau_D^{(I)} \sim \frac{a^5}{MAd_0} \frac{\sqrt{2} \beta^2}{\alpha \epsilon} n^{\frac{3}{4} - 2\epsilon}
\]

This result implies critical slowing down in the region \( \frac{1}{2} \leq \epsilon < \frac{5}{4} \), which also includes the case \( R^{(I)}_\infty = O(1) \); \( R^{(I)}_\infty \) can be reached in a infinite amount of time, in a finite time or instantaneously according with the value of \( \epsilon \) with respect to \( \frac{5}{4} \).

We proceed to region II by assuming \( |t_A| = \frac{2 \beta R}{\alpha n^{\frac{1}{2}} - \eta} \) with \( \eta \geq 0 \). When \( \Delta_\infty = 0 \) we obtain:

\[
R^{(II)}_\infty \sim \gamma_\eta \left( \frac{12 \beta R}{\alpha} \right) \left( d_0 a^2 \right)^{\frac{1}{\eta}} n^{\frac{1}{2} + \frac{1}{\eta}} \tag{20}
\]

where \( \gamma_\eta = (2)^{\frac{1}{2}} \) if \( \eta \neq 0 \) and \( \gamma_0 = \left( 1 + \sqrt{1 - \frac{\alpha}{\beta R}} \right)^{\frac{1}{\eta}} \). One verifies that this solution goes over to \( R^{(I)}_\infty \) along the critical line, where \( \eta \to 0, \epsilon \to 0 \) and \( \alpha = \beta^2 = \beta^2_1 \). Notice that \( R^{(II)}_\infty \) always diverges with \( n \).

The estimate (20) is valid also when \( \Delta_\infty \neq 0 \); let us denote by \( R^{(II)}_\infty \) the radius in such a case. First notice that, in the limit \( n \to \infty \), from equation (16) one has:

\[
R^{(II)}_\infty \sim 2d_0 \frac{1}{\Delta_\infty},
\]

where \( \Delta_\infty \) is a function of \( n \). Then, from the conservation law (17) with \( V \sim N(R^{(II)}_\infty)^3 \), one obtains that \( \Delta_\infty \sim (\frac{d_0}{a})^{\frac{1}{2}} n^{-\frac{1}{2} - \frac{1}{\gamma_\eta}} \). This shows that indeed \( R^{(II)}_\infty \sim R^{(I)}_\infty \).

Let us summarize the results, starting with the case \( t_A > 0 \).

In region I when \( t_A \) is positive and \( 0 \leq \epsilon < \frac{1}{2} \) the \( C_A \to 0 \) limit goes over to the Lifshitz-Slyozov equation. In general, when \( t_A > 0, t_A^2 < 4C_A \) the equation \( f(R, \Delta) = 0 \) can exhibit the following behaviors: a) two real roots in \( R \) at fixed \( \Delta \), the smaller one being unstable, the larger stable; b) merging of the two roots; c) no roots \( f < 0 \). The system spans the three regimes in dependence on the value of \( \Delta \); when \( \Delta = 0 \) the case c) always holds. Notice that the configuration \( R = 0 \) is stable in all cases; we have not been able to determine explicit estimates for the roots.

When \( t_A < 0, t_A^2 < 4C_A \) the equation \( f(R, \Delta) = 0 \) has a single stable root for each \( \Delta \). Correspondingly, \( R = 0 \) is always unstable.

In region II the situation is qualitatively similar to the previous one, with \( R^{(II)}_\infty (C_A, t_A) > R^{(I)}_\infty (C_A, t'_A) \). At \( \Delta = 0 \) we have the exact solution:

\[
R^{(II)}_\infty = \left[ \frac{6|t_A|}{C_A} d_0 \left( 1 + \sqrt{1 - \frac{4C_A}{t_A^2}} \right) \right]^{\frac{1}{3}} \tag{21}
\]

We observe that the value \( R(\Delta) \) which solves the equation \( f(R, \Delta) = 0 \) is always decreasing with \( \Delta \); this is an obvious consequence of the conservation law (17).

Let us finally add some comments on the cross-links distribution. The average distance between them is \( l \sim qC^{-1} \sim n^{\frac{1}{2}} \). Above the critical line we find that \( R_\infty \) scales with \( n \) in a way such that the inequality \( R_\infty < l \) always holds; this shows the consistency of our solution in the low density limit. Below the critical line the scale \( l \) clearly determines an upper bound for \( R \).

Throughout the paper we assumed that the system has undergone cross-linking at a temperature much higher than the demixing temperature: this amounts to exclude frozen large scale concentration fluctuations.
5. Conclusions

We studied the effect of cross-links on the droplet growth through accretion, in the late stages of the dynamics, when corrections to the mobility associated with reptation can be disregarded and the dominant scale is larger than the Gaussian chain radius.

We determined the dynamics of a single phase bubble immersed in the modulated background. We also discussed the statistics of an assembly in the absence of interaction, i.e. in a regime of low density of bubbles.

A first result is that the microdomain size does not only depend on the elasticity constant $C$, as a mere inspection of the structure factor $S(q)$ would suggest, but depends also on the depth of quenching $t$. This emerges already when we determine the ground state solution (time-independent) associated with the Gaussian form $S^{-1}(q)$.

We obtained analytic results in the limit of small density of cross-links $n \gg 1$, but our treatment is valid for general $n$; the phase diagram is shown in Figure 1.

It turns out that $R_\infty$ exhibits a competition between different mechanisms: bulk energy, interface energy, effective potential of the bubble in the background. The interface energy does contribute to $R_\infty$ only in a region close to the critical line; on the contrary, the decay time is always dependent on the interface interaction.

In the region of main interest $(I, t < 0)$, where the uncross-linked system would phase-separate, we obtain that the coarsening process is pinned at a scale $R_\infty$. More precisely, the critical line of the ground state $-t_A \sim C_A^{\frac{2}{3}}$ has a precursor at the level of the bubble excitation: indeed below the line $-t_A \sim C_A^{\frac{2}{3}}$, $R_\infty$ diverges with $n$. Above $-t_A \sim C_A^{\frac{3}{4}}$, on the contrary, $R_\infty$ tends to zero, the faster the closer to the $t_A = 0$ axis. In practice, for finite $n$, $R_\infty$ spans a continuum range of values; in particular at the critical line one has $R_\infty \sim n^{\frac{1}{2}}$, but at $t = 0$ $R_\infty$ is always zero for every $n$. 

Fig. 1. — Phase diagram of the microdomain solution. $\gamma$: $t^2 = 4C$, critical line for the static, modulated solution; $\beta$: $t^2 \sim C_\beta^{\frac{3}{2}}$; $\alpha$: $-t \sim C_\alpha^{\frac{2}{3}}$. (a): $R_\infty \ll 1, \tau_D \ll 1$; (b): $R_\infty \ll 1, \tau_D \gg 1$; (c): $R_\infty \gg 1$; (d): Lifshitz-Slyozov behavior.
When $t > 0$, again in region I, the configuration $R = 0$ becomes stable, and a second solution $R' \neq 0$ can appear in a suitable range of the parameters $(C, t)$. $R'$ loses its stability as $\Delta$ decreases, but it can survive as $\tau \to \infty$. It is important to point out that in the limit $C \to 0$ above the line $t_A \sim C_A^3$ one recovers the Lifshitz-Slyozov equation.

A second result refers to the time behavior. In all cases, the transient (before relaxation to steady state) is characterized by diffusion-dominated coarsening ($R(\tau) \sim \tau^{\frac{1}{2}}$) as one can easily verify from the scaling of the equations (15) and (16).

In region I with $t < 0$ the relaxation time $\tau_D$ goes to zero above the line $-t_A \sim C_A^0$ (i.e. the system tends to instantaneously relax to the microdomains). Between the lines $-t_A \sim C_A^0$ and $-t_A \sim C_A^3$ we have a region of critical slowing down: $\tau_D$ diverges with $n$, while $R_\infty$ tends to zero or at the most is finite. The line $-t_A \sim C_A^3$ then separates two regimes characterized by the same behavior of the steady state ($R_\infty \to 0$), but with completely different long time behaviors (instantaneous versus divergent relaxation). For finite $n$ this means that $\tau_D$ tends to increase indefinitely upon crossing from above the line $-t_A \sim C_A^3$, while $R_\infty$ is close to zero: we are then in the vicinity of the instability threshold for $R_\infty$.

This work, as a first attempt to analytically determine the dynamics of cross-linked polymers, is based on simplifying assumptions: we disregard disorder as well as domain-domain interactions. A description in terms of a single, bounded domain is reasonable for a small enough volume fraction of the B phase. When domains extending over the size of the system have formed, other accretion mechanisms come into play, hydrodynamic modes in the first place [19]. Work is presently in progress to include hydrodynamic effects. If disorder is described, as in [6] and [7], by means of a screening length $\lambda_s$, it can be included in our treatment in the limit of small momenta $q < \lambda_s^{-1}$, the effect being a correction to $C_A$ and $t_A$ (at least to leading order).

From the present description it emerges that the spontaneous production of microdomains tends to enlarge the pure-phase coexistence region from the mean-field critical line to the line $-t_A \sim C_A^3$, because below such a line one finds spinodal decomposition. Interestingly enough, the static renormalization group result, giving a critical line at $-t_A \sim C_A^3$ [9], goes in the opposite direction. In fact critical fluctuations tend to restore the more symmetric mixed phase, while our dynamic solution, where a pure-phase microdomain is assumed, can drive the mixed phase to instability. In the renormalization group treatment this channel is not included, but on the other hand our results do not hold close to the critical point.

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References


[18] Here and in the sequel it is always understood that the value of $t_A$ is compatible with a mean field treatment.