

Coarsening Rates of Bicontinuous Structures in Polymer Mixtures

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ABSTRACT: We discuss the coarsening of domains in bicontinuous structure of aqueous polymer mixtures, driven by hydrodynamic flow. Taking into account the bending energy as a contribution to the interfacial energy, we derive a general expression for the coarsening rate in these mixtures. Examining the limiting behavior of small and large length scales, we find two regimes. For small length scales, the size of the domains (Λ) scales with time (t) as $\Lambda \sim t^{1/3}$, while at large length scales, the domain size scales with time as $\Lambda \sim t$. The crossover between the two regimes occurs at a particular length scale, the critical radius R_c , which is dependent on the bending rigidity k , and the interfacial tension of a flat interface γ_0 ($R_c = \sqrt{2k/\gamma_0}$). In the case of aqueous biopolymer mixtures, we predict this particular length scale to be in the micron range. This new general expression for the coarsening of domains in aqueous polymer mixtures can explain experimental results [Lorén et al. *Macromolecules* 2001, 34, 8117], which show the two regimes of coarsening with a crossover at 4 μm .

Introduction

It is a well-known phenomenon that (aqueous) polymer mixtures can phase separate into two distinct phases. The kinetics of phase separation has received a lot of attention over the years, both experimentally and theoretically. Although a lot of mechanisms that have been proposed contribute to a better view of the phase separation process, a full understanding is still incomplete. In this paper, we focus on the coarsening of domains due to hydrodynamic flow in bicontinuous structures. This hydrodynamic flow is induced by the interfacial energy of the system, which is in general calculated using the interfacial tension of a flat interface, neglecting any curvature dependence of the interfacial energy.¹ However, Helfrich² showed in 1973 that the interfacial tension is curvature-dependent and that bending contributions to the interfacial energy are also of importance. In biopolymer systems, these bending contributions are considerable, with bending rigidities up to $500k_bT^3$ (k_b is the Boltzmann constant and T the temperature). To give a full description of the interfacial energy of a curved interface in biopolymer systems, the bending rigidity of the interface has to be taken into account. We derive a general expression for coarsening in polymer mixtures by hydrodynamic flow, by including the bending rigidity as a contribution to the interfacial energy. Examining the limiting behavior of small and large length scales, we find two regimes for the coarsening rate.

When phase separation occurs, the mixture becomes inhomogeneous by fluctuations in the concentration, which grow to equilibrium concentrations of the two coexisting phases of the mixture. The properties of the components and the kinetics of phase separation determine the morphology (droplets, bicontinuous structures) of the mixtures during phase separation. If one of the components is able to gel, a specific morphology of the mixture can be “frozen” by controlling the temperature during the phase separation. Understanding the kinetics of phase separation makes it possible to control the

structure of phase-separated polymer systems, which affects both stability and macroscopic properties of those systems.

Phase Separation

When the mixture is quenched into the metastable region, phase separation will occur through nucleation and growth. For deeper quenches, into the unstable state of the phase diagram, all concentration fluctuations will lead to a decrease in the free energy, and spinodal decomposition occurs,⁴ which is mainly observed for biopolymer mixtures.^{5–11} The time evolution in spinodal decomposition can be divided into two regimes:¹ the early stage and the late stage of phase separation. In the early stage, the system starts to develop inhomogeneities in the densities, which develop in time. In the late stage, the interfaces obtain their own interfacial characteristics. As the system favors a low interfacial free energy, the interfacial area will be decreased by the merging of domains, which will coarsen as the late stage of the phase separation continues.

Coarsening of Domains

During the coarsening of the domains, different morphologies can evolve in time. In general, two different morphologies can be distinguished: the droplet morphology and the interconnected morphology, as depicted in Figure 1. Droplet morphologies are usually obtained for mixtures, in which the volume fraction of one of the two coexisting phases is very small. Mixtures that contain approximately equal volume fractions of both of the phases form interconnected structures during the late stage of the phase separation. Thus, dependent on the composition of the mixture, the mixture can evolve through different morphologies, with their own characteristic length scales, Λ , which change during time.

The structure evolution during the early stage of spinodal decomposition was already described by Cahn and Hilliard in 1958.¹² They describe the free energy for an isotropic system of nonuniform composition or density, which is given in terms of a local density and

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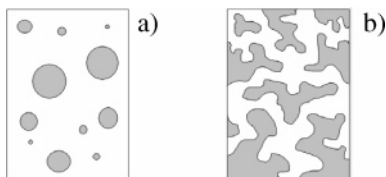


Figure 1. Morphologies that can be obtained during phase separation: (a) droplet morphology; (b) interconnected morphology.

the density gradients. This theory describes the time evolution of the density fluctuations, i.e., the stage of the phase separation during which particular wavelengths, Λ , grow in time. These growing wavelengths can be followed by light scattering by measuring the intensity at different wavevectors q . The term $\Lambda(q)$, known as the amplification factor, describes the coarsening of these fluctuations as a function of q . Plotting $\Lambda(q)/q^2$ vs q^2 , which is known as a Cahn–Hilliard plot, should yield a straight line in the early stage of the phase separation. This early stage of phase separation has been studied for several (bio)polymer mixtures, but for most mixtures this linear Cahn–Hilliard plot has not been observed.^{5,7,13,14} This feature seems to be a general characteristic for polymer solutions. This indicates that the theory of Cahn and Hilliard does not describe the structure evolution of the early stage or that the early stage of phase separation is probably too short to be measured during the time frame of the experiments. Since polymers are larger than simple molecules, the interfaces between the domains in polymer mixtures are much thicker than in simple binary liquids.³ The interfaces that are present in these mixtures can be viewed as interfacial regions, in which a concentration gradient for both (bio)polymers is present. Since the interfacial regions are relatively large and the gradients are relatively small, only small density fluctuations are needed to obtain these regions. Therefore, the formation of interfacial regions may be too fast to be measured with light scattering. This might explain why this regime is not observed by light scattering. As soon as the interfaces are formed, mass transport starts playing a role, which is a characteristic for the late stage of spinodal decomposition. This late stage is the more important regime for phase-separating (bio)polymer mixtures.

Coarsening Mechanisms

Late stage coarsening of the domains is characterized by a power law dependence of the domain size, $\Lambda \propto t^\alpha$, where α is an exponent, determined by the type of mass transport. In general, three different mechanisms are known:

(i) The evaporation–condensation mechanism (EC), or Ostwald ripening. In this mechanism, the bigger droplets grow at the expense of smaller ones by diffusion of material through the continuous phase into the larger droplets. This mechanism was described by Lifshitz and Slyozov in 1959.¹⁵

(ii) The Brownian–coagulation mechanism (BC), where the droplets move freely due to the Brownian motion and coalesce upon collision with another droplet. This mechanism was first described by Binder and Stauffer in 1974.¹⁶

(iii) Coarsening due to hydrodynamic flow (HF). In this mechanism, described by Siggia,¹ the flow in

bicontinuous regions is driven by the gradient in the capillary pressure.

The driving force for phase separation for the first two mechanisms is the diffusion of material (EC) or droplets (BC). The coarsening of the domains with time for both mechanisms is described by $\Lambda \propto t^{1/3}$.^{15,16} For the HF mechanism, the coarsening of the domains is driven by capillary forces. The coarsening of the domains is described by $\Lambda \propto t^1$.¹

The BC mechanism assumes the droplets move freely by Brownian motion and collide with another droplet. The EC mechanism ignores the interactions between droplets. Because of these assumptions, both mechanisms are valid only in the limit of small volume fraction. Coarsening through diffusion is obtained only for phase separating mixtures that evolve through a droplet-type morphology. When the volume fraction of the dispersed phase becomes higher, hydrodynamic flow fields start playing an important role. For these higher volume fractions, the HF mechanism is the more appropriate one. Coarsening via hydrodynamic flow is thus obtained in phase separation mixtures that evolve through interconnected patterns (volume fraction close to 0.5). Since the volume fraction, and thus the domain geometry, determines the coarsening of phase separation, one would expect one dominating exponent for a specific volume fraction; either $1/3$ for diffusive growth in droplet morphologies or 1 due to hydrodynamic flow for interconnected structures. However, literature reports several crossover regimes from one exponent to the other.^{7,9,13,17,18} During the past decade, several explanations for these crossover regimes have been proposed.

Nikolayev et al.^{19,20} explain a crossover from $1/3$ to 1 in off-critical mixtures by coalescence limited by hydrodynamics. For high volume fractions, elongated structures may be obtained, where the hydrodynamics play an important role. Tanaka^{21,22} describes a similar mechanism for the crossover from $1/3$ to 1 in off-critical mixtures. He states that droplets experiencing a collision have a much higher probability of a subsequent collision with a third neighboring droplet. This mechanism is called collision-induced collision. He also mentions a second mechanism that might be important at higher volume fractions, which is known as the interface quench effect. Contrary to a crossover from $1/3$ to 1, a crossover from 1 to $1/3$ has also been observed experimentally.^{23,24} This reduction in the growth rate has been explained by “pinning”.^{25,26} Pinning occurs when a bicontinuous microstructure is transformed into a droplet type pattern due to the breakup of the interconnected structures. When the structures break up into discrete droplets due to Rayleigh instabilities, the diffusion process might dominate over the hydrodynamic flows and cause the growth rate to decrease (from an exponent of 1 to an exponent of $1/3$). These coarsening mechanisms can explain a crossover from $1/3$ to 1 for mixtures that evolve through droplet morphologies and a crossover from 1 to $1/3$ for mixtures with interconnected patterns.

Comparison with Experimental Data

Recently, Lorén et al.²⁷ studied the late stage phase separation of a gelatin/maltodextrin sample of different concentrations and different quenches. For a 4% (w/w) gelatin and 7.3% (w/w) maltodextrin mixture, they report CLSM pictures taken during the entire process.

The pictures show interconnected structures, in which the interfacial region continues to be very large throughout the entire phase separation process (micron range). They measured the growth rate for the coarsening patterns and found an exponent of $1/3$ for small length scales and an exponent of 1 for larger length scales. The crossover from $1/3$ to 1 was observed at approximately $4\ \mu\text{m}$. The authors conclude that the first part of the evolution is governed by diffusion. However, the diffusion mechanisms are valid only for small volume fractions, i.e., droplet morphologies. Because interconnected structures are observed throughout the entire process, the volume fraction exceeds the volume fraction still applicable for the diffusion process. Therefore, the exponent $1/3$ (and subsequently the crossover from $1/3$ to 1) cannot simply be explained by the diffusion mechanisms or other mechanisms such as the collision-induced collision mechanism, the interface quench effect, or pinning.

In the next section, we will show that this crossover between $1/3$ and 1 in bicontinuous structures can simply be explained by hydrodynamic flow. We derive a new expression for the hydrodynamic flow, by taking the bending rigidity of the interfaces as a contribution to the interfacial energy. As a result, we obtain two regimes with a crossover at a particular length scale R_c .

Contribution of Bending Rigidity to Hydrodynamic Flow

Interfacial tension measurements show that biopolymer mixtures show near-critical behavior in a large concentration regime.^{28–30} Depending on the concentration quench into the phase diagram, and subsequently the location of the mixture on the tie line, these mixtures can evolve via droplet or interconnected morphologies. When the system is situated in the middle of the tie line, one obtains near-critical systems that evolve through interconnected structures. For this type of morphology, the coarsening rate is determined by the capillary instability of the domains. The interfacial energy induces a flow field in the domains, described by the Navier–Stokes equation

$$\rho \frac{\partial \vec{v}}{\partial t} + \rho(\vec{v} \cdot \nabla \vec{v}) = -\nabla \vec{P} + \rho \vec{g} + \eta \nabla^2 \vec{v} \quad (1)$$

in which \vec{v} is the flow velocity, ρ the density of the fluid, P the thermodynamic pressure, g the gravitational constant, and η the viscosity of the fluid. For biopolymer mixtures in steady flow (i.e., $\partial \vec{v} / \partial t = 0$), the $(\vec{v} \cdot \nabla \vec{v})$ term and the gravitational term ($\rho \vec{g}$) can be neglected. The Reynolds number, Re , can be estimated by $\rho \Lambda \vec{v} / \eta$. Assuming Poiseuille flow in the bicontinuous structures¹ of length l , we can write $Re = \rho \Lambda^2 \gamma / \eta^2 l$. Using $\eta \sim O(10^{-2})$ Pa s, $\rho \sim O(10^3)$, $\Lambda \sim O(10^{-6})$, $\gamma \sim O(10^{-6})$, and $l \sim O(10^{-5})$, we find that $Re \sim O(10^{-5})$; i.e., viscous effects dominate inertial effects. Using the above, the equation of motion can be written in the following form:

$$0 = -\nabla \vec{P} + \eta \nabla^2 \vec{v} \quad (2)$$

Since both the pressure and the velocity depend on the curvature of the domains, and the curvatures are related to the size of the domains (Λ), as the only relevant length scale, we approximate the pressure gradient by $\Delta P / \Lambda$. Here, ΔP denotes the difference in pressure over a distance Λ (the background pressure is taken constant and its gradient 0). The Laplacian of the

velocity can be approximated by v / Λ^2 . Substituting this into eq 2, one arrives at

$$\eta \frac{v}{\Lambda^2} \approx \frac{\Delta P}{\Lambda} \quad (3)$$

In this equation, the velocity is the time derivative of the domain size ($v = d\Lambda / dt$). The difference in pressure (ΔP) is determined by the interfacial tension, γ , and Λ ($\Delta P \propto \gamma / \Lambda$). Since the interfaces of the domains are not flat but curved, we express the interfacial tension in terms of its curvature. Using a van der Waals approach, Helfrich² derived the following expression for the curvature-dependent interfacial tension

$$\gamma(J, K) = \gamma_0 + k C_0 J + \frac{1}{2} k J^2 + \bar{k} K \quad (4)$$

in which γ_0 is the interfacial tension of a flat interface, k is the bending rigidity, C_0 is the spontaneous curvature of the interface, and \bar{k} is the rigidity constant associated with the Gaussian curvature. J and K are the total curvature and the Gaussian curvature, respectively. Assuming that the spontaneous curvature is zero, neglecting $\bar{k} K$, and substituting $J = -2 / \Lambda$, the interfacial tension can be given by

$$\gamma(\Lambda) = \gamma_0 + \frac{2k}{\Lambda^2} \quad (5)$$

The first term signifies the stretching contribution to the interfacial energy, and the second term signifies the bending contribution. Thus, the interfacial tension that causes the flow field and subsequently the coarsening of the domains can be divided in two different terms. The stretching contribution, which can be viewed upon as the interfacial tension of a flat interface, is size independent. However, the second term, which describes the bending contribution, is dependent on the curvature and thus on the size of the local curvature of the bicontinuous structures. The smaller these structures are, the larger their curvature is, and the larger the relative importance of the bending contribution is. Combining eqs 3 and 5, we obtain

$$\frac{d\Lambda}{dt} \approx \frac{\gamma_0}{\eta} + \frac{2k}{\eta \Lambda^2} \quad (6)$$

which leads to the following expression for the coarsening of the domains of a phase-separating mixture

$$\Lambda - R_c \arctan\left(\frac{\Lambda}{R_c}\right) \approx t \frac{\gamma_0}{\eta} \quad (7)$$

where $R_c (= \sqrt{2k / \gamma_0})$ is the crossover length scale where the stretching and the bending terms in eq 5 are equal. For $\Lambda \ll R_c$, the function $\arctan(\Lambda / R_c)$ can be approximated by $\Lambda / R_c - \Lambda^3 / R_c^3$. For $\Lambda \gg R_c$, $\arctan(\Lambda / R_c)$ approaches $\pi/2$. Taking the limits of small and large length scales, we obtain two regimes for the coarsening of the domains.

$$\frac{\Lambda \eta}{\gamma_0} \propto t \quad \Lambda \gg R_c \quad (8a)$$

$$\frac{\Lambda^3 \eta}{6k} \propto t \quad \Lambda \ll R_c \quad (8b)$$

So, in the limit of $\Lambda \gg R_c$, the domain size scales with time as $\Lambda \propto t$, which is equivalent to the scaling of the HF mechanism, in which only the curvature-independent interfacial tension is taken into account. Since we included the bending rigidity, we obtain a different expression in the limit of $\Lambda \ll R_c$, for which the coarsening scales as $\Lambda \propto t^{1/3}$. At length scales where the stretching term dominates, the coarsening exponent will be 1, while at length scales where the bending contribution dominates the coarsening exponent will be $1/3$. The crossover between the regimes occurs at $\Lambda \approx R_c$. The larger the bending rigidity and the smaller the interfacial tension of the interfaces between the separating domains, the larger this crossover length scale is.

Scholten et al.³ recently showed that for near-critical phase-separated biopolymer mixtures the bending rigidity is relatively large ($500k_bT$). Since the interfacial tension of these mixtures is very low, and the bending rigidity is large, the length scales for which the bending contribution dominates increases significantly compared to other systems. From a scaling relation, Scholten et al.³ showed that for these near-critical systems the crossover length scale, for which the bending dominates the stretching energy, is of the order of a micron. So, taking into account the bending rigidity of the curved interfaces, for near-critical biopolymer systems we expect to find a crossover from a coarsening exponent of $1/3$ to an exponent of 1 at a length scale in the order of a micron.

From the results of Lorén et al.²⁷ we can conclude that the phase separation of the gelatin/maltodextrin mixtures evolves through interconnected structures throughout the whole process. For this morphology, the process is driven by the hydrodynamic flow in the domains, but the HF mechanism cannot explain the crossover. However, our description of the hydrodynamic flow including the bending rigidity *does* explain a crossover between the exponents. They²⁷ found that the crossover between the exponents occurs at a length scale of approximately 4 μm , which is of the same order of magnitude as we predicted from scaling. Thus, taking into account the bending rigidity, we are able to explain these experimental results, which cannot be explained by any other described mechanism.

Conclusion

We have shown that for near-critical biopolymer systems the scaling of the domain size with time during the late stage of phase separating mixtures changes with time. For mixtures that contain a high volume fraction of the dispersed phase, hydrodynamic flow determines the coarsening of the domains in the phase separation process. We derived a general expression for the hydrodynamic flow that includes the bending rigidity of the interface and obtained a new description for the coarsening of the domains. Taking the limits $\Lambda \gg R_c$ and $\Lambda \ll R_c$, we found that the domain size with time scales as $\Lambda \sim t^{1/3}$ for small length scales and as $\Lambda \sim t$

for larger length scales. The crossover between these two exponents occurs when the stretching contribution to the interfacial energy equals the bending contribution. The crossover length scale, R_c , is equal to $\sqrt{2k/\gamma_0}$, which in the case of biopolymer mixtures can be expected to be in the micron range. This new description for coarsening by hydrodynamic flow can explain the crossover that is observed for mixtures that evolve through interconnected structures throughout the entire phase separation process.

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