Network formation in viscoelastic phase separation

Hajime Tanaka, Takehito Koyama and Takeaki Araki

Institute of Industrial Science, University of Tokyo, Meguro-ku, Tokyo 153-8505, Japan

E-mail: tanaka@iis.u-tokyo.ac.jp

Abstract
Viscoelastic phase separation is a new type of phase separation, which may
be universal in any dynamically asymmetric mixture composed of slow and
fast components. In such a dynamically asymmetric mixture, phase separation
generally leads to the formation of a long-lived 'interaction network' (transient
gel) of the slow components if the concentration is high enough and the attractive
interactions between the components are strong enough. Then, domains rich
in fast components are nucleated in a transient gel and they grow. Transiently,
a network pattern of the phase rich in slow components is produced even if it
is a minority phase. This is a unique feature of viscoelastic phase separation.
Pattern evolution is basically controlled by the nucleation kinetics of domains
rich in fast components under elastic interactions, the volume shrinking kinetics
and the self-induced elastic stress. We discuss the roles of bulk and shear
stresses on pattern formation and the mechanisms of network formation.

1. Introduction

Phase-separation phenomena are widely observed in various kinds of condensed matter
including metals, semiconductors, superconductors, simple liquids and complex fluids such
as polymers, surfactants, colloids, emulsions and biological materials [1]. Phase-separation
phenomena play key roles in the pattern evolution of immiscible multicomponent mixtures
of these materials. Phase separation in condensed matter has so far been classified into solid
and fluid models. However, in polymer solutions we recently found a new type of phase
separation, which can be explained by neither of these models [2–6]. Since viscoelastic modes
play a crucial role in this type of phase separation, we call it 'viscoelastic phase separation'. We
believe that viscoelastic phase separation should be universal in any dynamically asymmetric
mixture composed of fast and slow components [6–9]. Such 'dynamic asymmetry' can be
induced by either a large size difference or a difference in the glass transition temperature
between the components of a mixture. The former difference often exists in complex fluids
such as polymer solutions, micellar solutions, colloidal suspensions [8], emulsions and protein

solutions. The latter difference, on the other hand, in principle exists in mixtures of any material [6].

In dynamically asymmetric mixtures, phase separation generally leads to the formation of a long-lived 'interaction network' (transient gel) of slow-component molecules (or particles), if attractive interactions between them are strong enough and the concentration is high enough [9]. Then, droplets rich in fast components are nucleated in a transient gel and grow with time. In this regime, domain shape is determined by the elastic force balance condition. We emphasize that the self-induced mechanical stress in a transient gel plays a crucial role in pattern evolution. Differently from the case of a permanent (or chemical) gel, where the bulk and the shear modulus are not independent of each other, they can be rather independent in a transient gel, reflecting that in a transient gel bonds may be reconnectable for shear deformation but not for bulk deformation. Furthermore, the loss of the connectivity transforms a transient gel into an ordinary viscoelastic fluid. This feature is absent for physical and chemical gels. Thus, a variety of patterns can be formed during phase separation, depending upon the ratio of the shear modulus and the bulk modulus and their relaxational characteristics. Here we consider the roles of bulk and shear stresses on pattern evolution on the basis of both experimental and numerical studies [10, 11]. We also discuss mechanisms of network formation.

2. Experimental study: two types of network-like patterns

The samples used were mixtures of monodisperse polystyrene (PS) and diethyl malonate (DEM). The polymer solutions were sandwiched between two cover glasses, whose spacing was set to several micrometres. Although pattern evolution is crucially dependent upon the thickness of a sample film, here we do not discuss this interesting feature which is characteristic of elastic systems. After a temperature quench, pattern evolution was observed using phase-contrast microscopy.

Here we show two types of network patterns observed in polymer solutions, presumably formed by different mechanisms. One is observed in a polymer solution near a critical concentration ϕ_c, while the other is observed in a solution with a much more dilute polymer concentration. We call the former 'type A' and the latter 'type B'. In the initial stage of phase separation, a rather uniform 'microscopic' transient gel is formed for type A solutions, while for type B solutions polymer-rich droplets are formed by droplet spinodal decomposition and then their aggregation leads to the formation of a 'mesoscopic' network structure. For the latter case, therefore, the thickness of the network arms is comparable to the size of the initially formed droplets. This difference in the mechanism can be seen in the difference in the smoothness of the interface: reflecting the initial formation of droplets in type B, the network structure has a rougher interface for type B than for type A (see figure 1). The phase-separation process after this formation of a transient gel is basically similar for the two cases, although there is a difference in the volume shrinking kinetics. It is worth noting that according to our rheological studies the transient gel formed in the initial stage of phase separation is intrinsically 'transient' and nothing to do with ordinary physical gelation. In other words, phase separation is a prerequisite for transient gel formation.

3. Numerical study

To elucidate the physical mechanisms of formation of type A and B networks, we have performed two types of simulations: coarse-grained two-fluid simulations for type A and colloid simulations for type B.
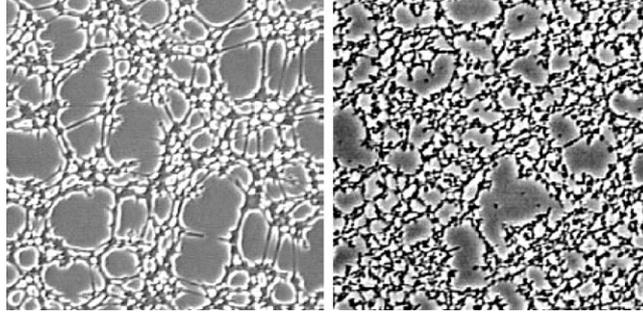
Figure 1. Left: type A. Network pattern observed in a critical mixture of PS and DEM ($M_w = 7.06 \times 10^5$, $\phi = 4.05$ wt%) after 5 min from a quench into $T = 11\,°C (T_c = 21.5\,°C)$. Right: type B. Network pattern observed in a mixture of PS and DEM ($M_w = 8.49 \times 10^6$, $\phi = 0.41$ wt%) after 50 min from a quench into $T = 15\,°C (T_{ps} = 28.0\,°C)$. The critical composition and temperature were $\phi_c = 1.2$ wt% PS and $T_c = 29.2\,°C$, respectively. One side of each photograph corresponds to 556 μm.

3.1. Coarse-grained two-fluid model: type A mechanism

Here we consider

(i) how we can physically describe transient gel formation and
(ii) how a network-like pattern is produced during the volume shrinking process of a transient gel.

Our coarse-grained simulations are based on a 'two-fluid' model of a mixture of polymer p and solvent s [1, 12–14]. Let $\vec{v}_p$ and $\vec{v}_s$ be the average velocities of polymer and solvent respectively, and $\phi(\vec{r}, t)$ be the concentration of polymer at a point $\vec{r}$ and time t. We employ the standard mixing free energy functional given by $F_{mix}\{\phi, T\} = \int d\vec{r}\,[k_B T\{\phi \ln\phi + (1 - \phi)\ln(1 - \phi) + \chi\phi(1 - \phi)\} + \frac{C}{2}|\vec{\nabla}\phi|^2]$. Here k_B is Boltzmann's constant, T is the temperature, C is a constant, and χ is the interaction parameter. The kinetic equations are given by

$$\frac{\partial \phi}{\partial t} = -\vec{\nabla} \cdot (\phi\vec{v}_p) + \theta, \tag{1}$$

$$\vec{v}_p - \vec{v}_s = -\frac{1 - \phi}{\zeta}[\vec{\nabla} \cdot \mathbf{\Pi} - \vec{\nabla} \cdot \boldsymbol{\sigma}], \tag{2}$$

$$\rho_0 \frac{\partial \vec{v}}{\partial t} \simeq -\vec{\nabla} \cdot \mathbf{\Pi} + \vec{\nabla} \cdot \boldsymbol{\sigma} - \vec{\nabla}\tilde{p} + \eta_s \nabla^2 \vec{v}, \tag{3}$$

where θ represents the thermal concentration noise, ζ is the friction constant between polymer and solvent, η_s is the viscosity of the solvent and ρ_0 is the density. Here $\vec{v}$ is the averaged velocity field of the solution and is given by $\vec{v} = \phi\vec{v}_p + (1 - \phi)\vec{v}_s$. $\tilde{p}$ is a pressure which is determined to satisfy the incompressible condition, $\vec{\nabla} \cdot \vec{v} = 0$. $\mathbf{\Pi}$ is the thermodynamic osmotic stress tensor. Note that $\vec{\nabla} \cdot \mathbf{\Pi} = \phi\vec{\nabla}\frac{\delta F_{mix}}{\delta\phi}$.

Most essential features of viscoelastic phase separation originate from the rheological constitutive equation of a mixture, which is necessary to close the above sets of equations [7, 9]. $\boldsymbol{\sigma}$ is the viscoelastic stress tensor, which should be supported solely by polymers and not by solvent molecules. Thus, the associated deformation can be expressed only by $\vec{v}_p$. Although only the shear part of the viscoelastic stress was considered in the original two-fluid model [13] for polymer solutions, we introduced the bulk stress in addition to the shear stress [7, 9–11] to describe transient gel formation and demonstrated [10, 11] that the bulk part of viscoelastic

stress plays an key role in pattern evolution. Thus, we express the total stress as $\boldsymbol{\sigma} = \boldsymbol{\sigma}_B + \boldsymbol{\sigma}_S$, where the suffixes B and S mean the bulk and shear stresses respectively. Note that the bulk stress $\boldsymbol{\sigma}_B$ stems from the motion of the polymer. Thus, it is intrinsically of mechanical origin and cannot be included in $\boldsymbol{\Pi}$. We assume that the shear stress obeys the following upper-convective Maxwell equation, $\frac{D}{Dt}\boldsymbol{\sigma}_S = \boldsymbol{\sigma}_S \cdot \vec{\nabla}\vec{v}_p + (\vec{\nabla}\vec{v}_p)^T \cdot \boldsymbol{\sigma}_S - \frac{1}{\tau_S(\phi)}\boldsymbol{\sigma}_S + G_S(\phi)\{\vec{\nabla}\vec{v}_p + (\vec{\nabla}\vec{v}_p)^T\}$, where $\frac{D}{Dt} = \frac{\partial}{\partial t} + \vec{v}_p \cdot \vec{\nabla}$ and τ_S and G_S are a relaxation time and a modulus of the shear stress respectively. Note that $(\vec{\nabla}\vec{v}_p)_{ij} = \partial_i v_{pj}$. To make the shear stress a traceless tensor, we redefine $\boldsymbol{\sigma}_S$ as $\boldsymbol{\sigma}_S = \boldsymbol{\sigma}_S - \frac{1}{d}\mathrm{Tr}\,\boldsymbol{\sigma}_S \boldsymbol{I}$, where $\boldsymbol{I}$ is a unit tensor and d is the space dimensionality. Since the bulk stress is isotropic, on the other hand, it can be expressed by a scalar variable, namely, $\tilde{\sigma} = \frac{1}{d}\mathrm{Tr}\,\boldsymbol{\sigma}_B$. Then, the bulk stress obeys the following equations: $\frac{D}{Dt}\tilde{\sigma} = -\frac{1}{\tau_B(\phi)}\tilde{\sigma} + G_B(\phi)\vec{\nabla}\cdot\vec{v}_p$ and $\boldsymbol{\sigma}_B = \tilde{\sigma}\boldsymbol{I}$. Here, τ_B and G_B are a relaxation time and a modulus of the bulk stress respectively.

It is quite difficult to make any theoretical prediction about the mechanical properties of a transient gel because of its intrinsically nonequilibrium nature. From both experimental observation and physical consideration, however, we argue that a polymer solution transiently behaves as a gel just after the temperature quench and the destruction of this transient gel is the process of the selective nucleation of a solvent-rich phase [9]. Thus, we express the formation and relaxation of a transient gel by using the following form for the bulk stress: $G_B \propto \Theta(\phi - \phi_0)$ and $\tau_B \propto \phi^2$, where Θ is a step function. The physical relevance of the above form of the bulk stress was discussed in detail in [7, 9]. Here we just emphasize that the bulk stress is the result of the 'connectivity' of polymers due to interpolymer attractions and induces the significant stress–diffusion coupling. For the shear mode, we assume the relations $G_S \propto \phi^2$ and $\tau_S \propto \phi^2$ for simplicity.

We numerically solve the basic equations described above. Details of the simulation methods are described in [10, 11]. A typical process of pattern evolution shown in figure 2, which captures all the essential features of network-forming phase separation observed in experiments (see figure 1). The stress distribution and its temporal change are also shown in figure 2. In figure 3 we plot the temporal change in the strength of three types of forces, osmotic force, bulk and shear mechanical forces. It is clear that the bulk stress tries to cancel out the osmotic stress (note that the sign of these two forces is opposite). This should be called 'stress-induced suppression of diffusion', which is a result of the stress–diffusion coupling: due to the connectivity, diffusion inevitably creates bulk stress and is thus mechanically suppressed. Note that the bulk stress has a peak slightly after the peak of $-\frac{1}{\Phi_p}\frac{\partial \Phi_p}{\partial t}$ (Φ_p being a volume fraction of the polymer-rich phase), which is a measure of the average bulk deformation rate $\langle\vec{\nabla}\cdot\vec{v}_p\rangle$. The peak of the shear mechanical force is, on the other hand, retarded from that of the bulk one. As can be seen in figure 2, it corresponds to a time when the network is broken up. This reflects the fact that the shear deformation rate is maximum during this process of network break-up. In the final stage, both mechanical stresses relax to zero since a transient gel becomes an ordinary viscoelastic fluid after losing the connectivity. Our numerical study has revealed that the bulk stress originating from the connectivity of the 'interaction network' plays a crucial role in the volume-shrinking behaviour of a polymer-rich phase and the resulting phase inversion, while the shear stress plays a crucial role in the formation of a well-developed network structure.

3.2. Colloid simulations: type B mechanism

We developed a new method (fluid–particle dynamics (FPD) method) to simulate the phase-separation dynamics of colloidal suspensions including hydrodynamic interactions [15].
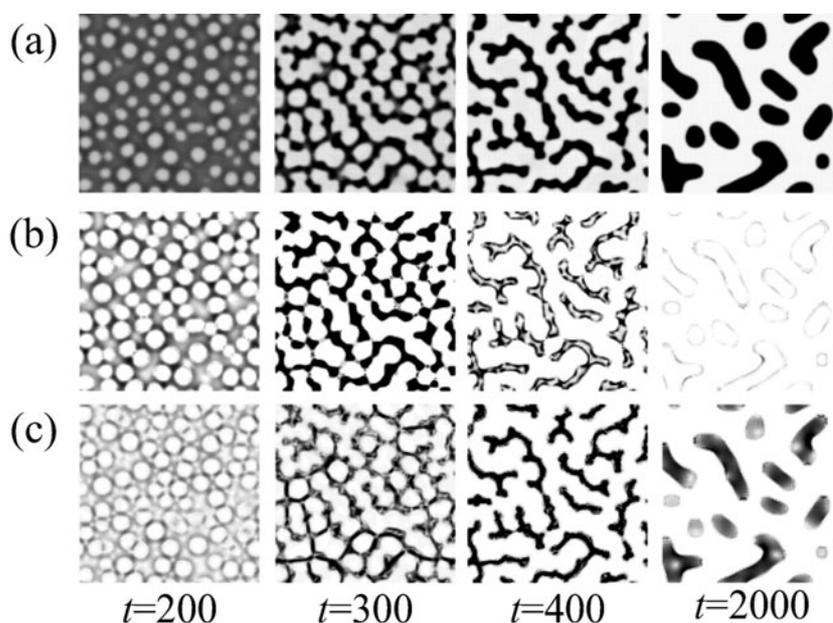
Figure 2. (a) Temporal change in the concentration field. The darker phase is polymer-rich. (b) The strength of the bulk stress (darker contrast = stronger stress). Bulk stress becomes strongest around $t = 300$, where the osmotic stress becomes strongest and thus the bulk deformation rate also becomes maximum. (c) The strength of shear stress. Shear stress becomes strongest around $t = 400$, where the network is broken up and thus the shear deformation rate becomes maximum. In this simulation $\phi_0 = 0.35, k_B T = 1.3, \chi = 2.7, C = 1.0, G_B = 5.0\Theta(\phi - \phi_0), \tau_B = 10.0\phi^2, G_S = 1.0\phi^2, \tau_S = 50.0\phi^2, \eta_S = 0.1, \zeta = 0.1$. We put the Gaussian concentration noise, the amplitude of which is 1.0×10^{-3}, for the initial state. The time step was $\Delta t = 0.02$ and the system size was 128×128.
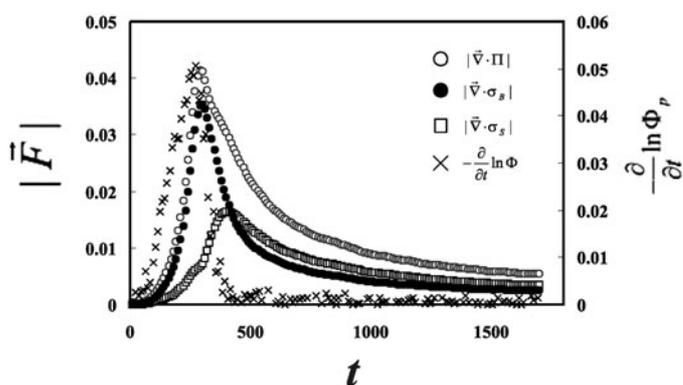
Figure 3. Temporal changes of three forces, osmotic and bulk and shear mechanical forces, and the volume shrinking rate, $-\frac{\partial \ln \Phi_p}{\partial t}$, during viscoelastic phase separation shown in figure 2.

In figure 4 we show the formation process of a transient gel in a colloidal suspension. The formation of a transient gel in colloidal suspensions strongly suggests that a transient gel state is indeed the percolated network of slow components, and thus viscoelastic phase separation should also take place in colloidal suspensions [8, 9]. We speculate that this mechanism
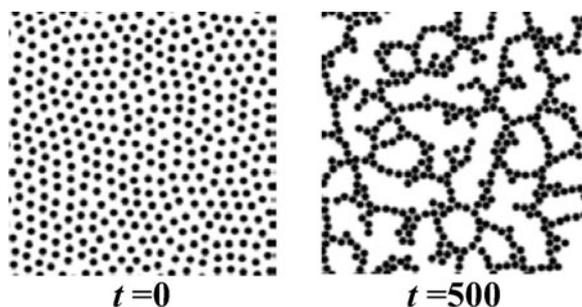
Figure 4. A transient gel formed in the aggregation process of colloid particles (FPD simulation). $\phi = 0.326$, the number of particles was 400, the system size was 256×256 and the viscosity ratio between colloid particles and the surrounding fluid was $R = 50$ ($\eta_c = 25.0$ and $\eta_s = 0.50$). The time step was $\Delta t = 0.01$. The parameters of the Lennard-Jones potential were $\epsilon = 0.25$ and $\sigma = 3.7$. See [15] for the meanings of the above parameters.

of mesoscopic network formation should be essentially the same as that of type B network formation in a dilute polymer solution (see the right-hand side of figure 1). This new mechanism of transient network formation due to aggregation of droplet-like objects may play an important role in phase separation of colloidal suspensions, emulsions and protein solutions.

4. Summary

We have demonstrated, by both experiments and simulations, that there are two different types of mechanism that produce network structures in viscoelastic phase separation. We argue that the basic features of viscoelastic phase separation of polymer solutions shown in this paper, which originate from transient gel formation, should be common to any dynamically asymmetric fluid mixtures such as emulsions, colloidal suspensions and protein solutions. Further studies are highly desirable to check this prediction. Finally, we note that this dynamic asymmetry and the resulting stress–diffusion coupling leads to the emergence of a new characteristic length scale, the so-called viscoelastic length [12, 13], in addition to the correlation length of the order parameter. We point out that the competition of these two lengths can even seriously affect the critical phenomena in a one-phase region of a dynamically asymmetric mixture [5, 16–18].

Acknowledgment

References

[1] Onuki A 2002 *Phase Transition Dynamics* (Cambridge: Cambridge University Press)
[2] Tanaka H and Nishi T 1988 *Japan. J. Appl. Phys.* **27** L1787
[3] Tanaka H 1992 *Macromolecules* **25** 6377
[4] Tanaka H 1993 *Phys. Rev. Lett.* **71** 3158
[5] Tanaka H 1994 *J. Chem. Phys.* **100** 5323
[6] Tanaka H 1996 *Phys. Rev. Lett.* **76** 787
[7] Tanaka H 1997 *Phys. Rev.* E **56** 4451
[8] Tanaka H 1999 *Phys. Rev.* E **59** 6842

[9] Tanaka H 2000 *J. Phys.: Condens. Matter* **12** R207
[10] Tanaka H and Araki T 1997 *Phys. Rev. Lett.* **78** 4966
[11] Araki T and Tanaka H 2001 *Macromolecules* **34** 1953
[12] Brochard F and de Gennes P G 1977 *Macromolecules* **10** 1157
[13] Doi M and Onuki A 1992 *J. Physique* II **2** 1631
[14] Taniguchi T and Onuki A 1996 *Phys. Rev. Lett.* **77** 4910
[15] Tanaka H and Araki T 2000 *Phys. Rev. Lett.* **85** 1338
[16] Tanaka H and Miura T 1993 *Phys. Rev. Lett.* **71** 2244
[17] Tanaka H, Nakanishi Y and Takubo N 2002 *Phys. Rev.* E **65** 021802
[18] Kostko A F, Anisimov M A and Sengers J V 2002 *Phys. Rev.* E **66** 020803(R)