

Shear-Induced Phase Separation in Polymer Solutions

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We examine spinodal decomposition induced in sheared semidilute polymer solutions which were stable in quiescent states. We find a transverse elastic force acting on polymers. It causes a diffusive flux of polymers from lower to higher concentration regions in mechanical equilibrium. This mechanism can also explain formation of a slipping layer in capillary flows. The scattering amplitude is also calculated in weak shear.

Polymer solutions, which are homogeneous and transparent in quiescent states, can undergo phase separation when they flow in capillary tubes or between concentric cylinders.¹⁻³⁾ The spinodal temperature, at which polymer solutions become cloudy, was observed to be higher than that in quiescent states even by several tens of degrees. The shift, $(\Delta T)_s$, is marked only in the semidilute region and is a strongly increasing function of the shear rate $\dot{\gamma}$, the molecular weight M , and the polymer volume fraction ϕ . Undoubtedly the phase separation behavior should be radically influenced by some elastic effect arising from deformations of entangled polymers.

Initial theories naively assumed "thermodynamics in the presence of shear" in which the total free energy consists of the mixing free energy and some elastic free energy.¹⁻³⁾ Such treatments, however, have no firm theoretical basis and cannot adequately explain data.* Recently two papers by Helfand and Fredrickson⁴⁾ and by the present author⁵⁾ proposed dynamical approaches in which the phase transition under shear was examined as an instability of stationary solutions to some dynamic equations. However, they started with somewhat different dynamic equations and obtained very different conclusions. Afterwards Doi claimed⁶⁾ that the dynamic equations for polymer solutions should be essentially the same as those for gels. In the preceding paper⁷⁾ the present author has examined possible forms of the dynamic equa-

tions within a phenomenological framework using the principle of positive entropy production. In our scheme Doi's equations have turned out to follow from a plausible but unjustified assumption for the convective motion of a conformation tensor W_{ij} which represents anisotropic polymer deformations. The main purpose here is to explain the mechanism of shear-induced phase separation in the simplest case. It exists for a class of dynamic equations proposed in ref. 7.

We examine linear stability of a homogeneous state under shear flow against the following perturbations,

$$\begin{aligned}\phi &= \phi_0 + \delta\phi(y, t), \\ V_x &= \dot{\gamma}y + \delta V_x(y, t).\end{aligned}\quad (1)$$

The flow V is along the x axis and the shear direction is along the y axis. The small deviations $\delta\phi$ and δV are assumed to depend on space and time as $\exp(iqy - \Omega t)$, where $|q|$ is much smaller than the inverse polymer size and $|\Omega|$ is much slower than the inverse of the rheological time τ_d . Of course we should examine stability for general perturbations. Here the stress tensor $-\sigma_p$ due to polymer deformations simply satisfies

$$\sigma_{p_{xx}} - \sigma_{p_{yy}} = N_1(\phi, \dot{\gamma}_T), \quad (2)$$

$$\sigma_{p_{yy}} - \sigma_{p_{zz}} = N_2(\phi, \dot{\gamma}_T). \quad (3)$$

Here N_1 and N_2 are the usual normal stress differences given as functions of $\phi = \phi_0 + \delta\phi$ and $\dot{\gamma}_T \equiv \dot{\gamma} + \delta\dot{\gamma}$, where $\delta\dot{\gamma}$ is the deviation of shear defined by

* See a comment in ref. 5 written as its ref. 9.

$$\delta\dot{\gamma} = \frac{\partial}{\partial y} \delta V_x(y, t). \quad (4)$$

It is known experimentally⁸⁾ that $N_1 > 0$ and $|N_2/N_1| \ll 1$. The total shear stress $-\sigma$ is also given by the local relation,

$$\sigma = \eta(\phi, \dot{\gamma}_T) \dot{\gamma}_T, \quad (5)$$

where $\eta \equiv \eta_0 + \Delta\eta$ is the total shear viscosity dependent on ϕ and $\dot{\gamma}_T$, η_0 is the solvent viscosity, and $\Delta\eta (\gg \eta_0)$ is the viscosity due to polymer deformations.

Considering only long wavelength fluctuations and neglecting the gradient free energy in (I.1),* we rewrite the equation for the velocity field V , (I.20), as

$$\rho_0 \frac{\partial}{\partial t} V \equiv \nabla \cdot (\sigma_p - \pi \mathbf{l}) - \nabla p + \eta_0 \nabla^2 V. \quad (6)$$

Here \mathbf{l} is the unit tensor and $\pi = \pi_\phi + \pi_{el}$ is the osmotic pressure defined by (I.12), π_ϕ and π_{el} being the contributions from the mixing free energy f and the elastic free energy f_{el} , respectively. For the slow deviations (1) we may set $\partial V / \partial t \equiv 0$ and

$$\sigma \equiv \sigma_{pxy} + \eta_0 \frac{\partial}{\partial y} V_x = \text{const}. \quad (7)$$

Namely, the deviations $\delta\phi$ and $\delta\dot{\gamma}$ do not change the shear stress, so that they are related by

$$\delta\sigma = \left(\frac{\partial \sigma}{\partial \phi} \right)_\dot{\gamma} \delta\phi + \left(\frac{\partial \sigma}{\partial \dot{\gamma}} \right)_\phi \delta\dot{\gamma} = 0. \quad (8)$$

In the semidilute region we expect the scaling relation $\sigma = \phi^{\hat{p}} \Psi(\dot{\gamma}\tau_d)$, where \hat{p} is the exponent for the shear modulus (see (I.2)) between 2 and 3, and $\Psi(x) \sim x$ for $x \ll 1$ and $\Psi(x) \sim x^{0.2}$ for $x \gg 1$ from rheological measurements.⁸⁾ Therefore, we may rewrite (8) as

$$\phi \left[\frac{\partial}{\partial \phi} (\dot{\gamma}\tau_d) \right]_\sigma = -\hat{p} \Psi(\dot{\gamma}\tau_d) / \Psi'(\dot{\gamma}\tau_d) < 0, \quad (9)$$

where $\Psi' = d\Psi/dx > 0$. The dimensionless shear $\dot{\gamma}\tau_d$ thus decreases with increasing ϕ . In other words, the degree of polymer deformations, which is determined by $\dot{\gamma}\tau_d$, decreases in relatively polymer-rich regions and vice versa.

On the other hand, taking the divergence of (6), we may express the pressure p as

$$p = -\pi - \sigma_{pyy} + p_0, \quad (10)$$

where p_0 is the background pressure and $p_0 - p = \pi - \sigma_{pyy}$ is nothing but the pressure change due to polymers in the shear direction (including the normal stress effect).

As the equation for the volume fraction deviation we first use the linearized version of (I.19) which has been set up incorporating Doi's idea,

$$\frac{\partial}{\partial t} \delta\phi = -(\phi_0 / \zeta) q^2 [\delta\pi - \delta\sigma_{pyy}], \quad (11)$$

where ζ is the friction coefficient. The convection term vanishes from $q_x = 0$ to linear order. From (2) and (3) the deviatoric part of σ_{pyy} is written as

$$\sigma_{pyy} - \frac{1}{3} T_r \sigma_p = -\frac{1}{3} (N_1 - N_2). \quad (12)$$

We introduce

$$\hat{\pi}_{el} = \pi_{el} - \frac{1}{3} T_r \sigma, \quad (13)$$

on which there are no available experiments, however. We then find

$$-\delta p = \delta\pi - \delta\sigma_{pyy} = \phi f'' \delta\phi + \delta\hat{\pi}_{el} + \frac{1}{3} (\delta N_1 - \delta N_2), \quad (14)$$

where f'' is the second derivative of the mixing free energy density f with respect to ϕ and use has been made of (I.13) to have the first term. Now from (11) the diffusion constant D_\perp in the shear direction is

$$D_\perp = \zeta^{-1} [\phi^2 f'' + g_n], \quad (15)$$

with

$$g_n = \phi \left(\frac{\partial}{\partial \phi} \hat{\pi}_{el} \right)_\sigma + \frac{1}{3} \phi \left[\frac{\partial}{\partial \phi} (N_1 - N_2) \right]_\sigma. \quad (16)$$

Here ϕ_0 in (1) is imply rewritten as ϕ for simplicity. The derivatives with respect to ϕ in (16) should be taken with σ held fixed due to (8). We expect that the ratios, $A_{el} = \pi_{el}/N_1$, $A_r = \frac{1}{3} (T_r \sigma_p)/N_1$, $A_2 = N_2/N_1$, are nearly constants independent of ϕ and $\dot{\gamma}\tau_d$ and that $\hat{\pi}_{el} + \frac{1}{3} (N_1 - N_2) = (A_{el} - A_r + \frac{1}{3} - \frac{1}{3} A_2) N_1 > 0$ (see

* Equations in ref. 7 will be referred to as (I.n).

ref. 7). We introduce A_n by

$$g_n = -A_n N_1. \quad (17)$$

The definition of A_n is then

$$A_n = - \left(A_{el} - A_t + \frac{1}{3} - \frac{1}{3} A_2 \right) \phi \left(\frac{\partial}{\partial \phi} \ln N_1 \right)_\sigma > 0. \quad (18)$$

The positivity of A_n can be shown from (9) as follows. Let $N_1 \sim \phi^{\hat{p}} (\dot{\gamma} \tau_d)^\beta$ where $\beta \cong 2$ for $\dot{\gamma} \tau_d < 1$ and $\beta \sim 1$ for $\dot{\gamma} \tau_d > 1$; then, $\phi (\partial \ln N_1 / \partial \phi)_\sigma$ is equal to $-\hat{p}$ for $\dot{\gamma} \tau_d \ll 1$ and to $(1-5\beta)\hat{p}$ for $\dot{\gamma} \tau_d \gg 1$.

The diffusion constant D_\perp becomes negative and the homogeneous state must be unstable against the fluctuations (1) when $\phi^2 f'' < A_n N_1$ from (15) and (17). For theta or poor solvents we use the Flory-Huggins expression for f ,

$$f = (k_B T / a^3) \left[\frac{1}{N} \phi \ln \phi + \left(\frac{1}{2} - \chi \right) \phi^2 + \frac{1}{6} \phi^3 + \dots \right], \quad (19)$$

where a is the monomer size, N is the polymerization index, and χ is related to the theta and critical temperatures by

$$N^{1/2} \left(\frac{1}{2} - \chi \right) = (T - T_\theta) / (T_\theta - T_c). \quad (20)$$

Therefore, the instability occurs for $\frac{1}{2} - \chi < (\frac{1}{2} - \chi)_{spi}$ with

$$\left(\frac{1}{2} - \chi \right)_{spi} = -\frac{1}{2} \phi + \frac{1}{2} (a^3 / k_B T) \phi^{-2} A_n N_1, \quad (21)$$

where use has been made of $N\phi^2 \gg 1$. The second term of the right hand side of (21) serves to raise the spinodal temperature by the following amount,*

$$(\Delta T)_s \sim N^{1/2} (T_\theta - T_c) (a^3 / k_B T) \phi^{-2} N_1 \sim N^{1/2} (T_\theta - T_c) \phi^{\hat{p}-2} (\dot{\gamma} \tau_d)^\beta, \quad (22)$$

where $N_1 \propto \phi^{\hat{p}} (\dot{\gamma} \tau_d)^\beta$. Strikingly $(\frac{1}{2} - \chi)_{spi}$ can even be positive in the non-Newtonian case. Since $\tau_d \propto N^{3.4} \phi^{4.5}$ in theta semidilute regions,⁹⁾ $(\Delta T)_s$ increases very strongly with increasing N and ϕ .

* In ref. 5 we set $\hat{p}=3$ and $\beta=2$, which is not precise in view of $\hat{p}=2 \sim 2.5$ in experiments (ref. 9).

In the above calculation we have used Doi's choice $\alpha=1$, where α is an unknown parameter introduced in ref. 7. There is a class of possible dynamic equations parametrized by α . For general α the expression for D_\perp , (15), still holds if the definition of A_n , (18), is changed as

$$A_n = - \left[A_{el} + \frac{\alpha - \phi}{1 - \phi} \left(\frac{1}{3} - \frac{1}{3} A_2 - A_t \right) \right] \times \phi \left(\frac{\partial}{\partial \phi} \ln N_1 \right)_\sigma. \quad (23)$$

The A_n remains positive even for $\alpha=\phi$ (if $A_{el} > 0$) and the instability exists for any α .

It is then of great interest how the two phases emerge and coexist after onset of the instability. The simplest picture is to suppose a planar interface perpendicular to the y axis separating a dilute region and a semidilute region. Such a dilute region will act as a slipping layer resulting in a plug flow even if the layer thickness is thin. In this case, from balance of the normal pressure, we require

$$\pi_\phi + \pi_{el} - \sigma_{pyy} \cong 0, \quad (24)$$

in the semidilute region close to the interface. This condition may be expressed in terms of χ as

$$\left(\frac{1}{2} - \chi \right)_{coex} = -\frac{1}{6} \phi - \frac{1}{3} (a^3 / k_B T) \times \phi^{-2} (N_1 - N_2 + 3\hat{\pi}_{el}). \quad (25)$$

Remarkably, this coexistence temperature in shear is lower than the equilibrium coexistence temperature contrary to the case of the spinodal temperature. Here we are assuming $N_1 - N_2 + 3\hat{\pi}_{el} > 0$ as below (18).

In comparing (21) and (25) we note that the shear in the homogeneous state and that after domain formation are generally different and it is inhomogeneous in the latter case. However, in the Newtonian case, where $(\frac{1}{2} - \chi)_{coex} > (\frac{1}{2} - \chi)_{spi}$, a slipping layer may appear near the boundary before the bulk instability sets in. This phenomenon may be treated as nucleation of a slipping layer. Its formation is favored when shear is largest near the boundary as for capillary flows. In the extreme case of $(\frac{1}{2} - \chi)_{spi} > 0$, fine domains are expected to emerge in the bulk region. For deep quenches

we expect viscous gel-like balls in a less viscous medium. They move relatively in shear but are connected by entanglements. The effective viscosity should be considerably decreased.

The above story of the instability is very similar to that proposed by Noziers and Quemada¹⁰ to explain plug formation in a sheared suspension flow. They introduced an additional chemical potential contribution of the form $\frac{1}{2}\beta\dot{\gamma}^2$. It corresponds to the last two terms in (14) or μ_{ei} in ref. 5.

We should also seek the possibility of shear-induced phase separation in good solvents. In this case the bulk modulus $\phi(\partial/\partial\phi)\pi_\phi$ and the shear modulus are both proportional to $k_B T \xi^{-3}$ where $\xi \sim a\phi^{-3/4}$ is the blob size.⁹ However, the coefficient of the former is larger than that of the latter by the order of 10^2 . The instability criterion $\pi \sim N_1$ is crudely written as

$$(\dot{\gamma}\tau_d)^\beta \sim 10^2, \quad (26)$$

where $N_1 \propto (\dot{\gamma}\tau_d)^\beta$. The instability can occur only in the non-Newtonian case. However, the present author is not aware of any observation of the bulk instability in good solvents. The estimated value of 10^2 might be still too small or the transition might not exist.

The shear-induced phase separation can also be expected in polymer blends if the lengths of the two polymers are considerably different. It will occur even in homolog polymer mixtures, for example, mixtures of long polystyrene + short polystyrene.

Finally we calculate the scattering intensity $I_q = \langle |\phi_q|^2 \rangle$ in weak shear. In equilibrium it is of the form $I_q^{(0)} = k_B T \phi^2 / K [1 + (q/\kappa)^2]$ where $K = \phi \partial \pi / \partial \phi$ is the bulk modulus and κ is the inverse correlation length. To first order in $\dot{\gamma}$ we find

$$\begin{aligned} \Delta_q \equiv [I_q - I_q^{(0)}] / I_q^{(0)} \approx & \left[\frac{2(\alpha - \phi)}{1 - \phi} \phi \eta' - \frac{\zeta}{\kappa^2 + q^2} \right] \\ & \times \dot{\gamma} \hat{q}_x \hat{q}_y / K \left[1 + \left(\frac{q}{\kappa} \right)^2 \right], \end{aligned} \quad (27)$$

where α is the gel-like parameter explained

above (23), $\eta' = \partial \eta / \partial \phi$, and $\hat{q} = q^{-1} \mathbf{q}$ is the direction of the wave vector. In the semidilute region the first term soon exceeds the second in the first brackets of (27) since $\zeta \sim 6\pi\eta_0 a^2 / \phi^2$ (unless α is very close to ϕ). Further assuming $q \ll \kappa$ we find

$$\Delta_q \approx 14(\alpha - \phi)(E/K)(\dot{\gamma}\tau_d)\hat{q}_x \hat{q}_y, \quad (28)$$

where E is the shear modulus and $\tau_d \equiv \Delta \eta / E$. We propose (28) as a relation to determine α from scattering experiments. The I_q in weak shear is enhanced in the stretched direction for $\alpha > \phi$. Interestingly, this is contrary to the cases of usual binary mixtures and polymer gels under shear stress,¹¹ where the counterpart of (28) in gels is $\Delta_q \approx -2E(K + \frac{4}{3}E)^{-1}\dot{\gamma}\hat{q}_x \hat{q}_y$, $\dot{\gamma}$ being the shear strain.

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