Elastic Effects in the Phase Transition of Polymer Solutions under Shear Flow

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We introduce a tensor variable to describe chain deformations in the continuum limit. Then we set up a dynamic model and apply it to the problem of phase separation in polymer solutions under shear. Effects of chain deformations are shown to be crucial in the entangled case. A large shear-demixing effect is found in semidilute solutions in agreement with experiments.

The phase-separation behavior in polymer solutions can be drastically altered by shear flow. In particular, two groups[1,2] reported that flowing polystyrene solutions with high molecular weights of 2×10^6 became turbid at temperatures much higher than the spinodal (cloud point) temperature of quiescent solutions. The spinodal temperature shift thus obtained, $(\Delta T)_s$, would be several tens of degrees in the semidilute region, increasing strongly with increases of the molecular weight M, the volume fraction ϕ, and the shear rate S. The effect becomes small and complicated if the polymer volume fraction ϕ is close to the critical value ϕ_c and the molecular weight is moderate.[3,4] On the contrary, a large effect of shear-induced dissolution (extension of the one-phase region) was observed in mixtures of polymer plus polymer plus solvent.[5,6] In such ternary systems large effects of shear are rather natural because the order parameter is the relative composition between the two polymers and its time scale is very slow. However, the large size of $(\Delta T)_s$ in polymer plus solvent systems is really surprising in view of the much faster time scale of the relative collective motion between the polymer and the solvent.

It has been expected that, when chains are deformed in shear flow, some elastic effect should come into play to change the spinodal temperature. However, it has been difficult to construct a statistical-mechanical theory for such an effect because the polymer solution is far from equilibrium in shear. So far several authors developed *thermodynamics in the presence of shear*[1-4,7] assuming a generalized Gibbs free energy of mixing, which consists of the ordinary Flory-Huggins mixing free energy and an elastic free energy stored in the system due to chain deformations.[8] This thermodynamic approach, however, contains serious ambiguities, mainly because it has no firm theoretical basis, and led to some confusing results.[9] The aim here is to present a dynamical model which describes the phase transition of deformed polymers in solvent. Our principle is that physical properties in steady states should be studied by seeking and examining stationary states of such a dynamic model as in the case of low molecular weight binary mixtures under shear.[10] Flow effects on phase separation are still poorly understood in the polymer case, but their study will become in-

creasingly important in the future.

Before presenting our theory we give a crude argument as to why the elastic effect can be important in semidilute solutions. Let f_{el} be the elastic free energy per unit volume stored in deformed chains, which are assumed to be elongated to a length $R_\| = \lambda R_0$ in one direction in a θ solvent. Here $R_0 = aN^{1/2}$ is the equilibrium size, a being the monomer size and N being the polymerization index. Then the stored free energy per chain is $\frac{1}{2} k_B T \lambda^2$ in the dilute case, $\phi < \phi^*$, as is well known.[11] On the other hand, it is $\frac{1}{2} k_B T \lambda^2 N/N_e$ in the semidilute case, $\phi > \phi^*$, for mild deformations, $\lambda \lesssim 1$. Here N_e $(\sim \phi^{-2})$ is the monomer number between two consecutive entanglements with other chains and $\phi^* = N^{-1/2}$ is the overlapping volume fraction.[11] Then, multiplying the chain density $a^{-3}\phi/N$ to these estimations, we obtain

$$f_{el} \sim k_B T E \lambda^2 . \tag{1}$$

Here $E \sim a^{-3}\phi/N$ for $\phi < \phi^*$ and $E \sim a^{-3}\phi^3$ for $\phi > \phi^*$, as it should be (since $k_B T E$ is the elastic modulus due to polymers[11]). On the other hand, the mixing free energy f_0 in the Flory-Huggins theory is written for $\phi \ll 1$ in the form[11]

$$f_0 \cong k_B T a^{-3} [N^{-1}\phi\ln\phi + (\tfrac{1}{2} - \chi)\phi^2 + \tfrac{1}{6}\phi^3 + \cdots] , \tag{2}$$

where χ is the interaction parameter. For $\phi^* \lesssim \phi \ll 1$ the shift of the spinodal curve will be determined by a balance of f_{el} and the second term in the square brackets of (2). This leads to $|(\Delta\chi)_s| \sim a^3 E\lambda^2/\phi^2 \sim \phi\lambda^2$, where $(\Delta\chi)_s$ is the spinodal value of $\Delta\chi = \frac{1}{2} - \chi$. In the mean-field theory we have $N^{1/2}\Delta\chi = (T - T_\theta)/(T_\theta - T_c)$, where T_θ is the θ temperature and T_c is the critical temperature.[11] Thus,[12]

$$|(\Delta T)_s| \sim (T_\theta - T_c)(\phi/\phi^*)\lambda^2 . \tag{3}$$

In shear flow λ is of the order of the dimensionless shear $S\tau$, τ being the very long rheological (disentanglement) time.[13] The right-hand side of (3) can well be several tens of degrees if λ is not too small, because $T_\theta - T_c = 4.5 \times 10^3 M^{-1/2}$ deg in polystyrene cyclohexane.[14]

Next we proceed to explaining our theory. When

chains are deformed, it is convenient to introduce a new gross variable representing the degree of internal anisotropy as in the case of liquid crystals. Hereafter we restrict ourselves to the semidilute case $\phi > \phi^*$. Let $R_1^{\alpha}, R_2^{\alpha}, \ldots$ be consecutive entanglement points on the αth chain. They are envisaged as slip links through which the chain can pass freely.[15] We introduce the following tensor for the αth chain:

$$W_{ij}^{\alpha} = \frac{1}{N a^2} \sum_{l=1}^{g^{\alpha}} (R_{l+1}^{\alpha} - R_l^{\alpha})_i (R_{l+1}^{\alpha} - R_l^{\alpha})_j , \qquad (4)$$

where g^{α} is the number of entanglements on the αth chain. Then we divide the space into cells with linear dimension l_0 much longer than the polymer size $N^{1/2}a$. For each cell $\mathbf{n}$ we define

$$W_{ij}(\mathbf{n}) = \frac{1}{N_p(\mathbf{n})} \sum_{\alpha \in \mathbf{n}} W_{ij}^{\alpha} - \delta_{ij} , \qquad (5)$$

where summation is over chains in the cell $\mathbf{n}$ and $N_p(\mathbf{n})$ is the chain number in the cell $\mathbf{n}$. Our definition of W_{ij} is analogous to that of the order-parameter tensor for liquid crystals.[16] In equilibrium we assume that the vectors $R_{l+1}^{\alpha} - R_l^{\alpha}$ are independently Gaussian with variance $N_e a^2$, where $N_e \sim \phi^{-2}$. Then, for a given chain distribution $\{N_p(\mathbf{n})\}$, we have $\langle W_{ij}(\mathbf{n}) \rangle = 0$ and

$$\langle W_{ij}(\mathbf{n}) W_{kl}(\mathbf{n}') \rangle = N_{en}(\mathbf{n})^{-1} \delta_{\mathbf{n},\mathbf{n}'} (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) , \qquad (6)$$

where $N_{en}(\mathbf{n}) = N_p(\mathbf{n}) N / N_e$ is the number of chain parts between two entanglements in the cell $\mathbf{n}$. The distribution of W_{ij} tends to be Gaussian as the cell size increases such that $N_{en}(\mathbf{n}) \gg 1$. The free-energy increase due to deformations is thus given by

$$F_{el}/k_B T = \frac{1}{4} \sum_{\mathbf{n}} N_{en}(\mathbf{n}) W_{ij}(\mathbf{n})^2 . \qquad (7)$$

In the continuum limit we find

$$F_{el}/k_B T = \frac{1}{4} \int d\mathbf{r} E \, \mathrm{Tr} \mathbf{W}^2 , \qquad (8)$$

where E is defined in (1). This is the stored free energy in our scheme. The distribution $\exp(-F_{el}/k_B T)$ surely gives rise to the variance (6). The above form for F_{el} will be used for macroscopic deformations, although it has been derived for small fluctuations. This will be allowable for $S\tau \lesssim 1$. It should also be noted that, just after an infinitesimal affine deformation, $\mathbf{r} \to \mathbf{r} + \delta \mathbf{A} \cdot \mathbf{r}$, we have $\langle W_{ij} \rangle = \delta A_{ij} + \delta A_{ji}$. We may call $\mathbf{W}$ the deformation tensor.

The total free energy F is the sum of F_{el} and the usual free energy F_0 for ϕ and the velocity field $\mathbf{v}$:

$$F_0 = \int d\mathbf{r}[f_0(\phi, T) + \frac{1}{2} K(\nabla\phi)^2 + \frac{1}{2} \rho v^2] . \qquad (9)$$

Here $K \sim k_B T / a\phi$ from the scaling theory[11] and ρ is the mass density assumed to be constant. We then set up dynamic equations for W_{ij}, ϕ, and $\mathbf{v}$ regarding them as

independent variables. The equations for ϕ and $\mathbf{v}$ are

$$\frac{\partial}{\partial t}\phi = -\nabla \cdot (\phi \mathbf{v}) + \lambda_0 \nabla^2 (\mu_0 + \mu_{el}) + \theta , \qquad (10)$$

$$\rho \frac{\partial}{\partial t}\mathbf{v} = -\nabla_p - \phi\nabla\frac{\delta}{\delta\phi}F_0 + \nabla \cdot \sigma + \eta_s \nabla^2 \mathbf{v} + \zeta , \qquad (11)$$

where $\mu_0 + \mu_{el}$ is the chemical-potential difference between the polymer and the solvent consisting of the usual part $\mu_0 = \delta F_0 / \delta\phi$ and the elastic part

$$\mu_{el} = \frac{\delta}{\delta\phi}F_{el} = \frac{1}{4} k_B T (\partial E/\partial\phi) \mathrm{Tr}(\mathbf{W}^2) . \qquad (12)$$

The λ_0 and η_s are the kinetic coefficients related to the power spectra of the random source terms θ and ζ via the fluctuation-dissipation relations. From the scaling theory $\lambda_0 \sim a^2/6\pi\eta_s$ for $\phi \gtrsim \phi^*$. The incompressibility condition $\nabla \cdot \mathbf{v} = 0$ is imposed and is assured by the pressure p. σ is the stress tensor due to chain deformations to be defined in (15) below. If μ_{el} and σ are absent, the above equations reduce to those for the usual critical fluids.[10] Our key assumption here is that the elastic contribution appears only in the chemical-potential difference in the equation for ϕ. This has not been fully justified at the present level of the study, while there will be no objection to (11).

The relaxation time τ of W_{ij} is the rheological time given by $\tau_b (N/N_e)^{\alpha}$, where $\tau_b = 6\pi\eta_s\xi^3/k_B T$ is the relaxation time in a single blob with size $\xi = a/\phi$ (the distance between entanglements)[11] and $\alpha = 3.4$ experimentally.[17] When the velocity gradients $D_{ij} = \partial v_i/\partial x_j$ are weak and nearly stationary, we should have

$$W_{ij} \cong \tau[D_{ij} + D_{ji}] , \qquad (13)$$

irrespective of the details of the dynamic equation for W_{ij}. In this paper, in analogy to the dumbbell model,[8] we assume the following simple dynamic equation for W_{ij}:

$$\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla\right) W_{ij} = D_{ij} + D_{ji} + \sum_k (D_{ik} W_{kj} + D_{jk} W_{ki})$$
$$- \tau^{-1} W_{ij} + f_{ij} , \qquad (14)$$

where the first four terms represent the deformation by flow[18] and f_{ij} ($= f_{ji}$) are random source terms. We surely obtain (13) in steady, weak shear if f_{ij} are neglected.

Note that the reversible terms on the right-hand sides of (10), (11), and (14) must ensure that the equilibrium distribution be given by $\exp[-(F_0 + F_{el})/k_B T]$. Then the form of the stress tensor σ is uniquely determined as

$$\frac{\sigma_{ij}}{k_B T} = EW_{ij} + E\sum_k W_{ik} W_{kj} + \frac{1}{4}(E - \phi E')(\mathrm{Tr}\mathbf{W}^2)\delta_{ij} . \qquad (15)$$

Here only the first term will be important together with

(13) and the specific details of (14) are irrelevant in the following discussion for weak shear. From (13) the excess viscosity $\Delta\eta$ in the zero-shear limit turns out to be

$$\Delta\eta = k_B T E \tau . \tag{16}$$

Now let us consider small fluctuations around a homo-

geneous disordered state under a simple shear $\langle\mathbf{v}\rangle$ $= Sy\mathbf{e}_x$, $\mathbf{e}_x$ being the unit vector along the x axis. We neglect the nonlinear couplings among the fluctuations and the random source terms. Namely, we are in the mean-field scheme. Retaining only the first term on the right-hand side of (15) and using (13), we obtain to first order in the deviations,

$$\sum_j \frac{\partial}{\partial x_j} \sigma_{ij} \cong (\Delta\eta)\nabla^2 v_{1i} + \sum_j (\Delta\eta)' \left[\frac{\partial}{\partial x_j}\phi_1\right]\left[\frac{\partial}{\partial x_i}\langle v_j\rangle + \frac{\partial}{\partial x_j}\langle v_i\rangle\right], \tag{17}$$

where $\mathbf{v}_1 = \mathbf{v} - \langle\mathbf{v}\rangle$, $\phi_1 = \phi - \langle\phi\rangle$, and $(\Delta\eta)' = \partial(\Delta\eta)/\partial\phi$. Notice that the time scale of $\mathbf{v}_1$ is much faster than that of ϕ_1 and we are allowed to set $\partial\mathbf{v}/\partial t = 0$ in (11). If use is further made of $\nabla\cdot\mathbf{v}_1 = 0$, the Fourier transform of $\mathbf{v}_1$ may be related to that of ϕ_1 in the following form:

$$(v_{1x})_\mathbf{k} = ik_y(1 - 2\hat{k}_x^2)k^{-2}\chi_\mathbf{k}, \quad (v_{1y})_\mathbf{k} = ik_x(1 - 2\hat{k}_y^2)k^{-2}\chi_\mathbf{k}, \quad (v_{1z})_\mathbf{k} = -2ik_z\hat{k}_x\hat{k}_y k^{-2}\chi_\mathbf{k} . \tag{18}$$

Here $\chi_\mathbf{k} = (S\eta'/\eta)\phi_{1\mathbf{k}}$, $\eta = \eta_s + \Delta\eta$, and $\hat{\mathbf{k}} = k^{-1}\mathbf{k}$ represents the direction of the wave vector. Thus $\mathbf{v}_1$ arise from the concentration dependence of $\Delta\eta$. Then (10) may be linearized as

$$\left[\frac{\partial}{\partial t} - Sk_x\frac{\partial}{\partial k_y}\right]\phi_{1\mathbf{k}} = -(\lambda_0 k_B T)k^2[f'' + \mathcal{D}^2 g(\hat{\mathbf{k}}) + Kk^2]\phi_{1\mathbf{k}} , \tag{19}$$

where $\mathcal{D} = \tau S$ is the dimensionless shear and

$$g(\hat{\mathbf{k}}) = \tfrac{1}{2}E'' + E'(\tau'/\tau - \eta'/\eta) + (E'\eta'/\eta)(\hat{k}_z^2 + 4\hat{k}_x^2\hat{k}_y^2) \cong (6E/\phi^2)[-1 + \alpha(\hat{k}_z^2 + 4\hat{k}_x^2\hat{k}_y^2)] \quad \text{for } \phi \gg \phi^* . \tag{20}$$

The primes denote the differentiation with respect to ϕ and $\eta' = (\Delta\eta)'$. The second line of (20) has been obtained by assuming $\eta \propto (N\phi^2)^\alpha$ and $E \propto \phi^3$, whereas the behavior near the critical point is not simple.

Because the fluctuations with $k_x \neq 0$ are eventually suppressed by shear,[10] the instability is first triggered by the fluctuations varying only in the y axis. Using the Flory-Huggins form (2) for f_0, we find a very large shear-demixing effect for ϕ considerably larger than ϕ^*,

$$(\Delta T)_s = \tfrac{1}{2}A_s(T_\theta - T_c)(\phi/\phi^*)\mathcal{D}^2 > 0 , \tag{21}$$

where $A_s = 6a^3 E/\phi^3 \sim 1$. This is consistent with (3). The origin of this effect is rather simple. Against fluctuations varying in the y axis, the shear stress σ_{xy} is fixed up to first order in the deviations. Then the elastic chemical potential μ_{el} in (10) is a decreasing function of ϕ and $\partial\mu_{el}/\partial\phi < 0$ because $\mu_{el} \propto \phi^{-4}\sigma_{xy}^2$. This leads to enhancement of the fluctuations varying in the y axis. It should be stressed here that our scheme is inapplicable to the case $\mathcal{D} > 1$. In the semidilute case this regime is characterized by the non-Newtonian viscosity,[13] where E and τ would also depend on S.[19]

The scattering amplitude $I_\mathbf{k} = \langle|\phi_\mathbf{k}|^2\rangle$ can be calculated if the random source term θ in (10) is recovered on the right-hand side of (19). We write the equation of $I_\mathbf{k}$ in a dimensionless form by introducing $\mathbf{q} = \xi\mathbf{k}$, $\hat{I}(q)$ $= \xi^{-2}I_\mathbf{k}$, and $\tau^* = 1 - A_s\mathcal{D}^2 + (1 - 2\chi)/\phi$ with $\xi = a/\phi$:

$$\{2q^2[\tau^* + \alpha A_s(\hat{q}_z^2 + 4\hat{q}_x^2\hat{q}_y^2)\mathcal{D}^2 + K_0 q^2]$$
$$- \tau_b Sq_x \partial/\partial q_y\}\hat{I}(q) = 2q^2, \tag{22}$$

where $K_0 = a\phi K/k_B T \sim 1$, $\alpha = 3.4$, and $\hat{\mathbf{q}} = q^{-1}\mathbf{q}$. The

operator ($\propto \partial/\partial q_y$) represents the convection and can be important at long wavelengths,[10] $q < q_c = (\tau_b S)^{1/4}$ $\sim (N\phi^2)^{-\alpha/4}\mathcal{D}^{1/4}$. Since there is also another characteristic wave number $q_a = (\alpha A_s/K_0)^{1/2}\mathcal{D} \sim \mathcal{D}$, a new regime arises in the case $q_c \ll q_a$ or $\mathcal{D} \gg (N\phi^2)^{-\alpha/3}$. There, $\hat{I}(q)$ is anisotropic even for $q > q_c$ as

$$\hat{I}(q) \cong 1/[\tau^* + \alpha A_s(\hat{q}_z^2 + 4\hat{q}_x^2\hat{q}_y^2)\mathcal{D}^2 + K_0 q^2] . \tag{23}$$

The general behavior for $q < q_c$ is complicated and is the subject of future study. We only remark that the elastic effect enhances the fluctuations in the y axis, while it suppresses those in the z axis.

Also interesting will be domain structures emerging below the instability point.[20] They should be crudely lamellar, consisting of flat thin droplets, due to the angle dependence of $g(\hat{\mathbf{k}})$, Eq. (19), and the elongation by shear. The two phases will be a nearly pure solvent and a semidilute solution. Recall that, when the viscosity inside a droplet is much smaller than that outside the droplet, it can be greatly elongated into slender shapes before its breakup in shear.[21] A dynamical balance will be eventually attained between the droplet growth due to the phase separation and the breakup mechanism by shear.[20] Schmidt and Wolf observed that the macroscopic viscosity decreases abruptly after demixing in polymer-solvent systems.[3] They considered that droplets with a low viscosity act as a lubricant. This is in marked contrast to the case of low-molecular-weight fluids in which the macroscopic viscosity increases due to domains.[22]

When a semidilute solution passes through a capillary,

the phase separation will be first triggered near the boundary wall with increase of the flow rate or lowering of the temperature. This results in a layer nearly free from polymers near the wall leading to anomalous rheological effects. Our scheme also shows that the polymer density tends to increase at the center of the capillary and decrease near the wall even before the onset of the layer formation. Such effects are of great technological importance and have been speculated or observed without clear theoretical explanations.[23] Notice that Nozieres and Quemada[24] proposed a mechanism of plug formation in flowing suspensions on the basis of the assumption that the chemical-potential difference contains a contribution proportional to the square of the shear rate as in our scheme.

ance and σ_{xy} is the shear stress. This is in accord with (1) because of $\lambda \sim S\tau$ and (16). However, it was not clear whether the derivative of f_{el} with respect to ϕ should be taken with fixed shear rate or fixed shear stress. As a difficulty $\partial^2 f_{el}/\partial\phi^2$ is positive definite for $\phi \gg \phi^*$ in both of the two cases, $S = $const (Ref. 7) and $\sigma_{xy} = $const (Ref. 2). This leads to only shear-induced dissolution for $\phi \gg \phi^*$ in the thermodynamic theories apparently in disagreement with the experiments. (The theories were claimed to work well for $\phi \sim \phi^*$.)

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