

Large Fluctuations in Polymer Solutions under Shear

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We present a phenomenological theory for the dynamics of concentration fluctuations of polymer solutions in the presence of simple shear flow. A coupling between concentration fluctuations and stress exists in the system as a result of the concentration dependence of viscosity and normal stress coefficients. Linear analysis indicates that scattering is greatly enhanced by the flow, even at temperatures significantly above the equilibrium coexistence curve. This may explain experimental observations of turbidity above the equilibrium transition, but this would not be a true shift in the phase transition.

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Polymer insolubility, i.e., phase separation of a binary mixture of a polymer from a low molecular weight solvent, is characterized by a coexistence curve that is highly asymmetric (in volume fraction of polymer, ϕ). Below the transition two phases coexist. One is a dilute phase in which the polymer molecules are isolated and collapsed. The other is a semidilute phase in which the polymers are Gaussian (radius of gyration $R_g \sim N^{1/2}$) and are strongly overlapped, but the volume fraction of polymer is still quite small. The properties of a polymer solution near the critical point¹ are those of a system in the Ising universality class, with related N dependence.²

In recent years a number of reports have appeared that hydrodynamic flow fields are capable of producing dramatic changes in the phase separation behavior of polymer solutions.³⁻⁵ Greatly enhanced turbidity is observed in the presence flow, often at temperatures as high as 50°C above the equilibrium critical temperature. The interpretation of such findings has conventionally been that the flow field has shifted the phase transition to higher temperatures. A quasithermodynamic theory has been developed to describe the effects of flow on the demixing properties of polymer solutions,³ but it has no basis in statistical mechanics and neglects much of the physics that we believe to be essential to the observed phenomena. As will be discussed, there are reasons to expect greatly enhanced concentration fluctuations in polymer solutions under flow, so that the experimentally observed turbidity may not reflect an actual symmetry-breaking transition.

The above experimental observations for polymer solutions are quite remarkable when contrasted with the critical properties of (low molecular weight) binary fluid mixtures under shear.^{6,7} In the latter systems, flow is found to suppress concentration fluctuations and restore mean-field character to the symmetric transition. Furthermore, the critical point is shifted to lower, not higher, temperatures, and the shift is at most a few degrees.

A phase separation (effected by a quench into the unstable region, from an initial homogeneous state with only small, thermal concentration fluctuations) can be thought of as a condition whereby molecules in a mixture

flow up a concentration gradient. This is a result of the lower chemical potential at higher concentrations when below the spinodal. Let us discuss another mechanism whereby molecules can flow up a concentration gradient. Picture a system with a plane wave of concentration deviating from the average. Associated with the concentration inhomogeneity there will be an inhomogeneity of transport coefficients, specifically the shear viscosity and normal stress coefficients. Consider a polymer molecule, in the inhomogeneous background, that is in a state of extension greater than some average (manifest as greater than average contribution to the stress). In relaxing back to an equilibrium degree of extension, the parts of the molecule in the low viscosity region will move more than those parts mired in the high viscosity. Thus, the relaxation moves the molecule's center toward the higher concentration region. Of course, *at equilibrium* the final concentration state achieved cannot depend on the transport coefficients. The fluctuation-dissipation theorem guarantees that the flux of molecules moving up the concentration gradient by the above mechanism is exactly compensated by an extra flux down the concentration gradient during the birth of the molecule's fluctuation to high extension. However, *in a flow field* the molecules can be convected to a nonequilibrium steady state of extension—excess extension in some directions, and lower extension in others. Thus concentration waves in certain directions will have a tendency to grow (that may be greater or less than their tendency to dissipate by diffusion). In other directions dissipation of the waves is enhanced.

To go beyond these intuitive considerations we present a phenomenological treatment of polymer solutions under flow. Although the model is somewhat oversimplified, we believe it to contain the essential ingredients of a proper theory. Our description is a type of fluctuating hydrodynamics for one scalar, one vector, and one tensorial field: $c(\mathbf{r}, t)$, the monomer concentration; $\mathbf{u}(\mathbf{r}, t)$, the velocity of the solution; and $\sigma(\mathbf{r}, t)$, the “deviatoric” stress contributed by the polymer (stress in excess of the isotropic stress under no-flow conditions). The hydrodynamic equations that we employ are the fol-

lowing:

$$\frac{\partial c}{\partial t} = -\mathbf{u} \cdot \nabla c + \frac{\lambda}{k_B T} \nabla \cdot \left[c \nabla \frac{\delta H}{\delta c} \right] - \frac{\lambda}{k_B T} \nabla \nabla : \boldsymbol{\sigma} + \theta_c, \quad (1)$$

$$\rho \frac{\partial \mathbf{u}}{\partial t} = \mathbf{T}_\perp \cdot \left[-\rho \mathbf{u} \cdot \nabla \mathbf{u} + \eta_s \nabla^2 \mathbf{u} + \nabla \cdot \boldsymbol{\sigma} + (\nabla c) \frac{\delta H}{\delta c} + \theta_u \right], \quad (2)$$

$$\boldsymbol{\sigma} = 2\eta(\phi) \mathbf{e} - \Psi_1(\phi) \mathbf{e}^\nabla + 4\Psi_2(\phi) \mathbf{e}^2, \quad (3)$$

where \mathbf{T}_\perp is a transverse projection operator reflecting incompressibility ($\nabla \cdot \mathbf{u} = 0$), and the upper convected derivative is defined as⁸

$$\mathbf{e}^\nabla \equiv \frac{\partial}{\partial t} \mathbf{e} + \mathbf{u} \cdot (\nabla \mathbf{e}) - (\nabla \mathbf{u})^T \cdot \mathbf{e} - \mathbf{e} \cdot (\nabla \mathbf{u}), \quad (4)$$

with $\mathbf{e} = \frac{1}{2} [\nabla \mathbf{u} + (\nabla \mathbf{u})^T]$ the symmetric rate-of-strain tensor. We will use, according to convenience, the concentration c (monomers per unit volume) or volume fraction ϕ ($\phi = cv_m$, where v_m is the volume per monomer). The uniform polymer concentration is c_0 .

Equations (1) and (2) are similar to model H of critical dynamics,⁹ and were derived by projecting a microscopic Rouse¹⁰ description of polymer dynamics onto the variables $\{c, \mathbf{u}, \boldsymbol{\sigma}\}$. The first two terms on the right-hand side (RHS) of Eq. (1) arise from the usual convective and dissipative fluxes. H does not include the elastic part of the Hamiltonian, which is manifested in the third term on the RHS. This term, not present in model H , represents a diffusive flux arising from inhomogeneous elastic (polymeric) stresses in the fluid. For the linear analysis that follows, the chemical potential is given by $\delta H / \delta c = [\epsilon - a^2 \nabla^2] \delta c$, where from the random-phase approximation for polymer solutions,¹ $\epsilon = (N\phi_0)^{-1} + (1 - \phi_0)^{-1} - 2\chi$ and $a^2 = R_g^2 / 3N\phi_0$.¹⁰ The equilibrium spinodal occurs at the temperature where $\epsilon = 0$. For the Rouse model, the Onsager coefficients in the second and third terms of Eq. (1) are equal and are given by $\lambda = k_B T / \zeta$, where ζ is the monomer friction coefficient. We retain this equality for the present analysis, but note that a nonlinear theory would probably renormalize the two coefficients differently. The final term in Eq. (1) is a Gaussian white noise with covariance that satisfies the fluctuation-dissipation theorem. This covariance de-

pends on the variable c , but to lowest order in inhomogeneity or when application calls for averaging over fluctuations, c may be replaced by c_0 .

Equation (2) is identical to the corresponding equation of model H (ρ is mass density and η_s is solvent viscosity), except for the third term on the RHS that represents the polymeric contribution to the solution stress. To terms linear in the fluctuations the Gaussian white noise θ_u has a variance proportional to $\eta_s + \eta(\phi_0)$, where $\eta(\phi)$ is the polymer contribution to shear viscosity.

Equation (3) is a consecutive equation relating polymeric stress to the rate of strain and is known as the "second-order fluid."⁸ In addition to the Newtonian viscosity, it contains first and second normal stress coefficients, $\Psi_1(\phi)$ and $\Psi_2(\phi)$. Strictly speaking, $\Psi_2(\phi) = 0$ for the Rouse model, but we retain the possibility of a finite Ψ_2 since concentrated polymer solutions exhibit second normal stresses.

We will examine Eqs. (1)–(3) to terms linear in the amplitude of the inhomogeneity. In the absence of flow this is suitable for a study of the decay of small fluctuations, or to describe the early stages of spinodal decomposition. In the late stages nonlinear terms must be included to stabilize the system against the infinite growth of fluctuations. In the present case we will see that convection provides a stabilization mechanism. Nevertheless, the composition fluctuations are found to be extraordinarily large in particular regimes; and for such regimes it should be understood that the present linear analysis is inadequate. We write the viscosity and normal stress coefficients as

$$\eta(\phi) = \eta(\phi_0) + \eta' \delta \phi(\mathbf{r}), \quad (5)$$

$$\Psi_i(\phi) = \Psi_i(\phi_0) + \Psi_i' \delta \phi(\mathbf{r}). \quad (6)$$

In the absence of the inhomogeneity the velocity field is a simple shear flow, $\mathbf{u}(\mathbf{r}) = \kappa y \mathbf{e}_x$, where \mathbf{e} is a unit. Equations (2) and (3) may be used to calculate the flow pattern and deviatoric stress to lowest order in $\delta \phi$. Here we ignore $\partial / \partial t$, $\mathbf{u} \cdot \nabla$, and noise terms, assuming that the velocity and stress fields rapidly relax to the forms dictated by the local concentration pattern. Substituting into Eq. (1) yields an equation of motion for the Fourier components of the concentration fluctuations, $\phi(\mathbf{k})$, where we only consider \mathbf{k} in the x - y plane:

$$\frac{\partial \phi(\bar{\mathbf{k}})}{\partial \bar{t}} = \bar{\kappa} \bar{k}_x \frac{\partial \phi(\bar{\mathbf{k}})}{\partial \bar{k}_y} - \bar{\lambda} \Omega(\bar{\mathbf{k}}) \phi(\bar{\mathbf{k}}) + \bar{\theta}_\phi, \quad (7)$$

$$\Omega(\bar{\mathbf{k}}) = \bar{k}^2 [\bar{\epsilon} - h(\beta) + \bar{a}^2 \bar{k}^2], \quad (8)$$

$$h(\beta) = 2l_x l_y \bar{\kappa} \bar{\eta}' + l_x^2 \bar{\kappa}^2 \bar{\Psi}_1' + \bar{\kappa}^2 \bar{\Psi}_2' - [(l_x^2 - l_y^2) \bar{\kappa} \bar{\eta}' - l_x l_y \bar{\kappa}^2 \bar{\Psi}_1'] \frac{l_x^2 \bar{\kappa}^2 \bar{\Psi}_1 + 2(l_x^2 - l_y^2) \bar{\kappa}^2 \bar{\Psi}_2}{\bar{\kappa}(\bar{\eta} + \bar{\eta}_s) + l_x l_y \bar{\kappa}^2 \bar{\Psi}_1}. \quad (9)$$

Here β is the angle that \mathbf{k} makes with the x axis, $l_x = \cos \beta$, and $l_y = \sin \beta$. In these equations we have gone to dimensionless variables, denoted by an overbar and defined in Table I. Henceforth we shall omit the overbar except to distinguish between ϵ and $\bar{\epsilon}$. In all our calculations we assign a value to the variables based on a degree of polymerization $N = 2500$ and an average concentration $\phi_0 = 0.02$, which is the mean-field critical concentration.

TABLE I. Reduced parameter and values.

Reduced variables	Definition	Value (Rouse) ^a
\bar{t}	t/τ	
$\bar{\kappa}$	$\kappa\tau$	
\bar{k}	kR_g	
$\bar{\epsilon}$	$\epsilon N\phi_0$	
$\bar{\theta}_\phi$	$\theta_c v_m \tau$	
$\bar{\alpha}^2$	$\alpha^2 N\phi_0/R_g^2$	1/3
$\bar{\lambda}$	$\lambda\tau/NR_g^2$	1/6
$\bar{\eta}$	$\eta N\phi_0 v_m/k_B T\tau$	$N\phi_0^2$
$\bar{\Psi}_1$	$\Psi_1 N\phi_0 v_m/k_B T\tau^2$	$0.8N\phi_0^2$
$\bar{\Psi}_2$	$\Psi_2 N\phi_0 v_m/k_B T\tau^2$	0
$\bar{\eta}_s$	$\eta_s N\phi_0 v_m/k_B T\tau$	$1.29\phi_0/N$

^a $\tau = N_c R_g^2/6k_B T$, ζ =monomer friction constant $\approx 6\pi\eta_s v_m^{1/3}$, v_m =monomer volume $\approx 100 \text{ cm}^3/\text{mol}$, $R_g^2 = Nb^2/6$, and b =monomer statistical length $\approx 0.67 \text{ nm}$.

Equation (7) may be converted to an equation for the steady-state fluctuation intensity (the structure factor),

$$S(\mathbf{k}) = \langle \phi(\mathbf{k})\phi(-\mathbf{k}) \rangle,$$

which is proportional to the scattering intensity. The equation for S is

$$\left[2\lambda\Omega(\mathbf{k}) - \kappa k_x \frac{\partial}{\partial k_y} \right] S(\mathbf{k}) = 2\lambda k^2. \tag{10}$$

We have chosen a normalization (reduced units) for S such that in the absence of flow $S = (\bar{\epsilon} + \alpha^2 k^2)^{-1}$. The solution may be reduced to quadratures by the method of characteristics⁶

$$S(\mathbf{k}) = 2\lambda \int_{-\infty}^0 dt' \exp\left[-2\lambda \int_{t'}^0 dt'' \Omega(\mathbf{k}(t''))\right] k^2(t'), \tag{11}$$

$$\mathbf{k}(t) = k_x \mathbf{e}_x + (k_y - \kappa k_x t) \mathbf{e}_y. \tag{12}$$

To appreciate this formula note that in a pure shear field waves are convected in such a way that their wave vector changes length and rotates clockwise (β decreases). A wave that has wave vector \mathbf{k} at time 0 has or had wave vector $\mathbf{k}(t)$, given by Eq. (12), at time t . The content of

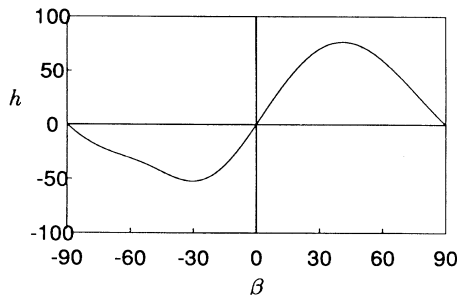


FIG. 1. Function $h(\beta)$ vs β for $\kappa=1$, indicating tendency toward growth of fluctuations for positive β .

Eq. (11) is that the fluctuations at \mathbf{k} at time 0 are composed of the fluctuations created at $\mathbf{k}(t')$ at all earlier times t' . These are created at a rate $2\lambda k^2(t')$ by the noise. They are also partially dissipated at each moment t'' between t' and 0. The rate of dissipation is proportional to Ω evaluated at the current wave vector, $\mathbf{k}(t'')$.

The function $h(\beta)$, through which the effects of the coupling of the elastic stress, velocity fluctuations, and concentration are manifest, is plotted in Fig. 1 for $\kappa=1$. In this strong-flow case h has a maximum at $h_{\max}=76.5$ corresponding to $\beta=\beta_{\max}=41^\circ$. To set the scale in physical terms, $\bar{\epsilon}=76.5$ might correspond to a temperature more than 100°C above the θ temperature for a typical polymer-solvent system.³ When the dissipation rate is large compared with the shear rate, i.e., $\lambda\Omega(\mathbf{k}) \gg \kappa$, then S is given by

$$S(\mathbf{k}) \approx \frac{1}{\bar{\epsilon} - h(\beta) + \alpha^2 k^2}. \tag{13}$$

For the most part the term $\alpha^2 k^2$ is negligible, and the scattering depends only on the angle of observation β . S is considerably more for β positive than the no-flow value of $1/\bar{\epsilon}$, and less for β negative.

When $\bar{\epsilon} < h_{\max}$, Eq. (13) cannot be valid in the region of β where $\bar{\epsilon} - h(\beta)$ is negative. In this region the fluctuations will be growing and the scattering at these angles will be enormous, as illustrated in Fig. 2. The convection plays an important stabilizing role in sweeping \mathbf{k} out of this region and into a region of smaller β where the fluctuation again dissipates. Even at β 's somewhat below the unstable region the fluctuations can be expected to be very large since they have not had sufficient time since passing through that region to decay back to values approaching Eq. (13). Although this mechanism for avoiding complete instability exists, the results are cer-

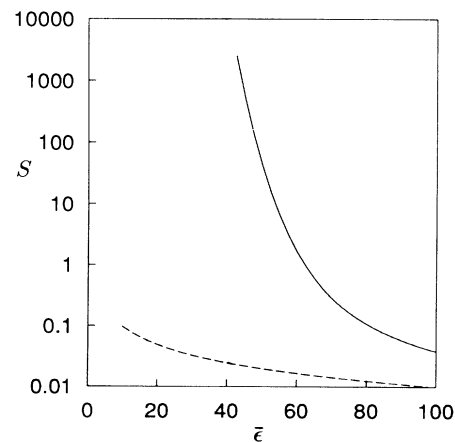


FIG. 2. Structure function S (\propto scattering) at $\beta=41^\circ$ (β_{\max}) and $|\mathbf{k}|=1$. The solid line, S for flow rate $\kappa=1$, is to be contrasted with the dashed line, which is the absence of flow. The figure shows growth of fluctuations with decreasing $\bar{\epsilon}$ (temperature) far above the spinoidal temperature ($\bar{\epsilon}=0$).

tainly quantitatively deficient because of the neglect of nonlinear terms. Without these terms the theory is really only adequate for $\bar{\epsilon}$ above h_{\max} , or perhaps to describe the early development of fluctuations in a spinoidal-decomposition-like T -jump experiment. The large fluctuations in the region $\bar{\epsilon} \lesssim h_{\max}$ might be sufficient to induce a first-order transition, even at the critical composition. Work on a nonlinear theory is in progress.

For smaller flow rates, with κ and $\epsilon = O(\phi_0)$, both the convection and the nonlocal term, $\alpha^2 k^2$, play a role. The full Eq. (11) is needed. Typical results will be discussed elsewhere.

Finally a word should be said about the special case of waves with \mathbf{k} totally in the y direction. Such waves are not convected [cf. Eq. (12)]. Thus, in principal, it should be possible to form a stable phase with the interface parallel to the x axis. From Fig. 1 we expect that the stability of such waves ($\beta = \pm \pi/2$) should not change at the no-flow transition temperature ($\epsilon = 0$). This is true only if the second normal stress coefficient is zero (or if it has no concentration dependence). With a negative Ψ_2 , as is usually the case, the prediction, using the Rouse model for other variables, is that the "transition" would move to higher ϵ (higher T). As a note of caution, using Zimm parameters¹⁰ the transition moves

to lower ϵ . However, even more caution is required because of the enormous fluctuations that were shown above to exist in the system. Such fluctuations are capable of shifting the transition significantly through renormalization.

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