Anisotropic suppression of phase separation in polymer solutions by oscillatory shear

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We consider the effects of subjecting a polymer solution to a simultaneous oscillatory shear flow and temperature jump into the two-phase region of the phase diagram. We predict that if the oscillatory shear stresses are significant enough then the flow suppresses phase separation in the flow direction, leading to the possibility of creating strongly aligned structures. We construct a quantitative dynamic phase diagram in the amplitude-frequency plane showing the conditions for the growth or decay of concentration fluctuations. Further, we discuss the time dependence of periodic structure factors in the flow-vorticity and flow-gradient planes. It is also shown that significantly enhanced scattering occurs at large scattering vectors regardless of whether the unbounded growth of fluctuations at smaller scattering vectors is suppressed.

I. INTRODUCTION

The effects of shear flow on polymeric systems have attracted considerable interest. This is partly due to its relevance to industrial polymer processing and partly due to such systems providing an ideal test of modern ideas in nonequilibrium statistical mechanics. A quantitative approach to characterizing the coupling between shear and structure involves the study of the response of the concentration fluctuations. Such fluctuations are quantifiable experimentally and may be determined theoretically. Concentration fluctuations are measured using scattering techniques, and a rich variety of behavior has been observed, such as shear-induced mixing and demixing [1–3], and enhanced scattering at finite wave vectors [4]. Anisotropic enhancement and/or growth of concentration fluctuations in polymer solutions is known to be induced by flows such as simple shear [5–11].

Much of the focus has been on the effects of steady state flows on polymer solutions, with the major theoretical advances, with regards to predicting structure factors being due to Milner [12] and Helfand and Fredrickson [13]. Recently, Saito and Hashimoto [14] studied a solution of ultrahigh molecular weight polystyrene in dioctyl phthalate (DOP) subjected to oscillatory shear flows using small-angle light scattering. They found that for large enough amplitudes of shear, the solution displayed features very similar to that of phase separation: "butterfly patterns" in the flow-vorticity plane were observed. Malevanets and Yeomans [15] have presented a lattice-Boltzmann scheme to numerically model binary systems with a viscosity difference between components, subjected to oscillatory shear flow. They observed the formation of persistent structures in the flow-shear gradient plane. Their observations of such structures are clearly in qualitative agreement with the experiments of Ref. [14]; however, direct comparison is not possible since the experiments and numerical calculations were carried out in different planes with respect to the flow direction. We recently developed a theory [16] to predict the structure factor arising from small concentration fluctuations in the presence of an oscillatory shear field. This simple model was used to calculate scattering in the flow-vorticity plane, and we showed that it may explain the underlying features observed in Ref. [14]. The model builds upon the approach of Doi and Onuki [17], who considered the effects of spatial stress gradients on the relaxation dynamics of concentration fluctuations. Such stress gradients arise naturally when fluctuations in concentration occur, since the stress in a polymer solution is strongly dependent on the concentration. It was shown, by using the principle of force balance, that the stress enters the equation of motion at the same level as the chemical potential. In Ref. [17] it was assumed that the response of individual polymers to shear flow could be described by a single relaxation time. The model has been modified to account for the rheological response of a binary blend in which each component has distinctly different relaxation times [18–20]. This approach gives rise to an explicit concentration dependence of the components of the stress tensor, which has important consequences even for a system in which the stress relaxation can be described by one dominant timescale.

In this paper, we extend the theory to consider the effects of subjecting a polymer solution to a simultaneous oscillatory shear flow and temperature jump into the two-phase region of the phase diagram. In Sec. II, we summarize the relevant results from our previous paper and present a simpler expression for calculating the structure factor, even within the one-phase region of the phase diagram. This development leads to a new prediction, which is discussed in Sec. III. We show that if the oscillatory shear stresses are significant enough then the flow suppresses phase separation in the flow direction. We derive an exact condition for the suppression of fluctuations and calculate the critical wave vectors below which fluctuations grow in both the flow-vorticity and the flow-shear gradient planes. We emphasize that the conditions are determined in terms of independently

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accessible properties of any given polymer solution and the control parameters of the applied oscillatory shear field. Thus, the quantitative predictions of this paper are amenable to experimental verification. Finally, in Sec. IV, we show growth rates and periodic structure factors for a range of conditions.

II. THEORY

We start by briefly reviewing the important ideas and theory covered in more detail in our previous paper [16]. The strain in oscillatory shear flow is described by $\gamma(t) = \gamma_0 \sin(\omega t)$, so that the velocity profile is

$$v_x = \gamma_0 \omega \cos(\omega t) y, \quad v_y = 0, \quad v_z = 0,$$

where x denotes the flow direction, y denotes the shear gradient direction, z denotes the vorticity direction, γ_0 is the maximum amplitude of the flow, and ω is the frequency. For a polymer solution, the important thermodynamic parameters are the difference between χ, the Flory-Huggins interaction parameter, and χ_S, its value on the quiescent spinodal, and κ, the interfacial energy. The important kinetic parameters are the collective mobility M, and a relaxation time τ_L of the polymer that, in terms of the tube model, is related to the idealized Doi-Edwards relaxation time $\tau_L^{(DE)}$ for the polymer in a matrix of fixed obstacles by $\tau_L = (1/2)\tau_L^{(DE)}$. Within our model two further parameters are required, the polymer volume fraction ϕ_L and G_L, the plateau modulus of the polymer. We assume incompressibility, such that $\phi_L + \phi_S = 1$, where ϕ_S is the volume fraction of the solvent.

Our starting point is [16] an equation of motion for fluctuations in the composition,

$$\frac{\partial \delta\phi_L(\mathbf{q},t)}{\partial t} = \theta(\mathbf{q},t) + \gamma_0 \omega \cos(\omega t) q_x \frac{\partial \delta\phi_L(\mathbf{q},t)}{\partial q_y}$$
$$- M \left[2q^2(\chi_S - \chi + \kappa q^2) \right.$$
$$\left. - \frac{q_i q_j}{k_B T \langle \phi_L \rangle} \frac{\delta\sigma_{ij}^{(n)}}{\delta\phi_L} \right] \delta\phi_L(\mathbf{q},t), \quad (1)$$

where $\delta\phi_L(\mathbf{q},t)$ is the deviation from the volume fraction in Fourier transform space, $\mathbf{q} = (q_x, q_y, q_z)^T$, and $\sigma_{ij}^{(n)}$ are the components of the stress tensor due to the deformation of the polymer network. The effects of thermal fluctuations are represented by $\theta = \theta(\mathbf{q},t)$, which we assume to be Gaussian white noise and to satisfy the fluctuation-dissipation theorem,

$$\langle \theta(\mathbf{q},t) \rangle = 0,$$

$$\langle \theta(\mathbf{q},t)\theta(\mathbf{q},t') \rangle = 2Mq^2 \delta(t-t').$$

From Eq. (1), we obtained, using the method characteristics, an equation of motion for the structure factor $S(\mathbf{q},t) = \langle |\delta\phi_L(\mathbf{q},t)|^2 \rangle$, in terms of reduced variables $\bar{G}_L = G_L/k_B T$, $\bar{q}^2 = q^2 M \tau_L$, $\bar{t} = t/\tau_L$, $\bar{\omega} = \omega \tau_L$, and $\bar{\kappa} = \kappa/M\tau_L$,

$$\frac{dS}{d\bar{t}} = \left\{ -4\bar{q}^2(\chi_S - \chi + \bar{\kappa}\bar{q}^2) + \frac{8\bar{q}_x\bar{q}_y\bar{G}_L\gamma_0}{1+\bar{\omega}^2}[\bar{\omega}^2 \sin(\bar{\omega}\bar{t}) \right.$$
$$\left. + \bar{\omega} \cos(\bar{\omega}\bar{t})] \right\} S + 2\bar{q}^2. \quad (2)$$

This equation was obtained on the basis of the linear viscoelastic model for the network stress,

$$\boldsymbol{\sigma}^{(n)} = \int_{-\infty}^{t} G(t-t') \left\{ 2\mathbf{e}(t') - \frac{2}{3}[\text{tr } \mathbf{e}(t')]\mathbf{I} \right\} dt', \quad (3)$$

where $G(t)$ is the stress relaxation function discussed in Ref. [16], $\mathbf{e}$ is the rate-of-strain tensor whose components are defined in terms of velocity gradients as $e_{ij} = 1/2(\boldsymbol{\nabla}_j v_{Li} + \boldsymbol{\nabla}_i v_{Lj})$, and $\mathbf{I}$ is the identity tensor. No effect of normal stresses has been considered and, therefore, spatial variations of the flow field are not important [12]. Hence, the dynamics are only governed by coupling between the fluctuations in polymer concentration and in the network stress.

In an oscillatory shear flow, the stress tensor Eq. (3) has only two equal components $\sigma_{xy}^{(n)} = \sigma_{yx}^{(n)}$, which represent shear stresses. In the adiabatic approximation, Eq. (3), coupled with the double reptation model for the stress relaxation function [21,22], leads [16] to an explicit relation between the shear stress and the concentration,

$$\sigma_{xy}^{(n)} = \frac{\phi_L^2 G_L \gamma_0}{1+\omega^2\tau_L^2}[\omega^2\tau_L^2 \sin \omega t + \omega\tau_L \cos \omega t], \quad (4)$$

which allows us to deduce the fluctuations in the stress straightforwardly. In fact, their contribution can be readily identified in Eq. (2).

The consequence of the oscillatory convection term in Eq. (2) is that the component of the wave vector in the shear gradient direction is not constant, and is described by $\bar{q}_y = \bar{q}_{y0} - \gamma_0\bar{q}_x \sin(\bar{\omega}\bar{t})$, where $\bar{q}_{y0}$ is fixed and chosen such that $\bar{q}_y$ has some desired value at a given time $\bar{t} = \bar{t}_1$. This expression is substituted into Eq. (2), which may then be solved for given $\bar{\mathbf{q}}_0 = (\bar{q}_x, \bar{q}_{y0}, \bar{q}_z)^T$; the solution yields the structure factor for $\bar{\mathbf{q}} = (\bar{q}_x, \bar{q}_y, \bar{q}_z)^T$, where the value of $\bar{q}_y$ depends on the temporal phase $\bar{\omega}\bar{t}_1$. For example, if it is the shear flow-vorticity plane which is of interest, i.e., $\bar{q}_y = 0$, then the structure factor at each time between $\bar{\omega}\bar{t}_1$ and $\bar{\omega}\bar{t}_1 + 2\pi$ requires a solution to Eq. (2) with a different value of $\bar{q}_{y0} = \bar{\gamma}_0\bar{q}_x \sin(\omega\bar{t}_1)$ ranging from $-\gamma_0\bar{q}_x$ to $\gamma_0\bar{q}_x$.

From Eq. (2), which is a first-order nonhomogeneous linear differential equation, we can write the time dependence of the structure factor as

$$S(\bar{\mathbf{q}},\bar{t}) = S_0(\bar{\mathbf{q}}_0)\exp\{F(\bar{\mathbf{q}}_0,0) - F(\bar{\mathbf{q}}_0,\bar{t})\}$$
$$+ \exp\{-F(\bar{\mathbf{q}}_0,\bar{t})\} \int_0^{\bar{t}} 2\bar{q}^2(t')\exp\{F(\bar{\mathbf{q}}_0,t')\}dt'. \quad (5)$$

The exponent of the integrating factor can be written explicitly as

$$F(\bar{\mathbf{q}}_0, \bar{t}) = A_0 \bar{t} - \frac{A_1}{\bar{\omega}}\cos\{\bar{\omega}\bar{t}\} + \frac{B_1}{\bar{\omega}}\sin\{\bar{\omega}\bar{t}\} - \frac{A_2}{2\bar{\omega}}\cos\{2\bar{\omega}\bar{t}\}$$

$$+ \frac{B_2}{2\bar{\omega}}\sin\{2\bar{\omega}\bar{t}\} - \frac{A_3}{3\bar{\omega}}\cos\{3\bar{\omega}\bar{t}\} + \frac{B_4}{4\bar{\omega}}\cos\{4\bar{\omega}\bar{t}\}. \tag{6}$$

The prefactors of the oscillatory terms in the solution, which depend on the conditions and $\bar{\mathbf{q}}_0 = (\bar{q}_x, \bar{q}_{y0}, \bar{q}_z)^T$, are defined in the Appendix. The prefactor of the term linear in time is given by,

$$A_0(\bar{\mathbf{q}}_0) = 4\bar{q}_0^2(\chi_S - \chi + \bar{\kappa}\bar{q}_0^2) + 2\gamma_0^2 \bar{q}_x^2(\chi_S - \chi) + 4\bar{\kappa}\left[\gamma_0^2 \bar{q}_x^2 \left(\bar{q}_0^2 \right.\right.$$

$$\left.\left. + 2\bar{q}_{y0}^2 + \frac{3\gamma_0^2 \bar{q}_x^2}{8} \right) \right] + \frac{4\bar{q}_x^2 \bar{G}_L \gamma_0^2 \bar{\omega}^2}{1 + \bar{\omega}}, \tag{7}$$

where $\bar{q}_0^2 = \bar{q}_x^2 + \bar{q}_{y0}^2 + \bar{q}_z^2$. In our previous work we solved Eq. (5) numerically with an initial condition $S_0(\bar{\mathbf{q}}_0)$, determined by the behavior of concentration fluctuations in the absence of shear. Unsurprisingly, we found that the solution became periodic after sufficient cycles. We can gain further insight into the behavior by noting that if a periodic solution for the structure factor exists then we must have the condition that $S(\bar{\mathbf{q}}, \bar{t} + 2\pi/\bar{\omega}) = S(\bar{\mathbf{q}}, \bar{t})$. Hence, from Eq. (5),

$$S(\bar{\mathbf{q}}, \bar{t}) = \frac{\exp\{-F(\bar{\mathbf{q}}_0, \bar{t} + 2\pi/\bar{\omega})\}}{1 - \exp(-2\pi A_0/\bar{\omega})}$$

$$\times \int_{\bar{t}}^{\bar{t} + 2\pi/\bar{\omega}} 2\bar{q}^2(t') \exp\{F(\bar{\mathbf{q}}_0, t')\} dt'. \tag{8}$$

Furthermore, the patterns in the flow-vorticity plane ($\bar{q}_y = 0$) are actually π periodic in the temporal phase $\bar{\omega}\bar{t}$ because structure factors with the same initial values $S_0(\bar{\mathbf{q}}_0)$ have been convected to $\bar{q}_y = 0$ from $\bar{q}_{y0} = \gamma_0 \bar{q}_x \sin(\omega \bar{t}_1)$ and from $-\bar{q}_{y0} = \gamma_0 \bar{q}_x \sin(\omega \bar{t}_1 + \pi)$. Therefore, for that plane the terms with $2\pi/\bar{\omega}$ in Eq. (8) could be substituted simply with $\pi/\bar{\omega}$. Note that the initial condition $S_0(\bar{\mathbf{q}}_0)$ is, in effect, hidden in the terms with A_0. In addition to being computationally less demanding than Eq. (5), since it is only necessary to integrate over one cycle of oscillatory shear, inspection of Eq. (8) leads to an unusual consequence, which we will focus our attention on in the following section.

III. SUPPRESSION OF PHASE SEPARATION IN THE FLOW DIRECTION

Clearly a physically meaningful solution to Eq. (8), i.e., a positive periodic structure factor, can only exist if the denominator is positive, or equivalently, if $A_0 > 0$. From Eq. (7), it can be seen that this will always be the case in the one phase region, i.e., when $(\chi_S - \chi) > 0$. If $A_0 < 0$ then the assumption that a periodic solution exists must be incorrect, which corresponds to the only other physically meaningful possibility that the structure factor grows without bound. This situation simply corresponds to the early stages of phase separation. Hence, as expected shear stresses in oscillatory

shear are not able to induce phase separation. On the other hand, if we now consider what happens inside the quiescent two-phase region, i.e., $(\chi_S - \chi) < 0$, then we see that the condition $A_0 < 0$ when a shear is applied does not coincide with the quiescent condition for phase separation. In the latter case the nature of the early stages of phase separation, based on Cahn-Hilliard theory [23], is well established. In the one-phase region of the phase diagram, fluctuations decay exponentially, $\delta\phi_L(\bar{\mathbf{q}}, \bar{t}) \propto \exp\{-R(\bar{\mathbf{q}})\bar{t}\}$, with a rate dependent on $\bar{\mathbf{q}}$ according to

$$R(\bar{\mathbf{q}}) = 2\bar{q}^2(\chi_S - \chi + \bar{\kappa}\bar{q}^2). \tag{9}$$

Above the critical condition defined by $\lim_{q \to 0} R(\bar{q}) = 0$, the rate becomes negative for $\bar{q}_c^2 < (\chi - \chi_S)/\bar{\kappa}$ and such fluctuations are unstable and grow. There is a fastest growing wave vector $\bar{q}_m^2 = (\chi - \chi_S)/2\bar{\kappa}$, which from above can be seen to grow at a rate $R(\bar{\mathbf{q}}_m) = -(\chi_S - \chi)^2/2\bar{\kappa}$.

The $\bar{\mathbf{q}}$ dependence of Eq. (7) is similar to the $\bar{\mathbf{q}}$ dependence of the growth (and decay) of fluctuations of Eq. (9) but with a directional dependence. Importantly, when $q_x \neq 0$, there are additional positive contributions to the rate which serve to act against the thermodynamic driving force for phase separation, hence stabilizing certain fluctuations that would otherwise grow without bound. The term driving the stability is the contribution arising from the energy due to the stress in phase with the strain, coupled to the convection. The relative magnitude of this term with respect to the other contributions, which serve to promote growth, is maximized when $\bar{q}_z = 0$. The terms arising from interfacial tension will always increase A_0, even in the presence of shear as would be expected, and such terms serve to suppress fluctuations at higher $\bar{\mathbf{q}}$, just as happens in usual phase separation. By analogy with the Cahn-Hilliard theory we are able to determine a new critical condition. In the flow direction ($\bar{q}_y = 0, \bar{q}_z = 0$) this is given by $\lim_{\bar{q}_x \to 0} A_0/\bar{q}_x^2 = 0$, from which the condition for the suppression of the growth of fluctuations becomes,

$$\frac{\bar{G}_L}{(\chi - \chi_S)} > \frac{(1 + \bar{\omega}^2)(2 + [1 + 2a]\gamma_0^2)}{2\gamma_0^2 \bar{\omega}^2}, \tag{10}$$

where $a = \sin^2(\bar{\omega}\bar{t}_1)$.

The requirement for the growth or suppression of fluctuations is illustrated in Fig. 1 for a variety of values of $\bar{G}_L/(\chi_S - \chi)$ as a function of shear amplitude γ_0 and frequency $\bar{\omega}$. The growth of fluctuations in the $\bar{q}_x = 0$ direction only continues when the amplitude and frequency of the oscillation are below certain values. The growth of fluctuations becomes suppressed for *all* temporal phases $\bar{\omega}\bar{t}_1$ when $a = 1$ in Eq. (10). For every other intermediate value of $a \in [0, 1]$ the growth would not be always suppressed. For some temporal phases the growth will continue from cycle to cycle, whereas for others it will remain periodic. Hence, a pair of γ_0 and $\bar{\omega}$ on the dynamic phase diagram (Fig. 1) define a particular curve in that intermittent region corresponding to a certain value of a and, thus, $\bar{\omega}\bar{t}_1$. Beneath that curve [for $\sin^2(\bar{\omega}\bar{t}) \leq \sin^2(\bar{\omega}\bar{t}_1)$] fluctuations will grow, above it [for $\sin^2(\bar{\omega}\bar{t}) > \sin^2(\bar{\omega}\bar{t}_1)$] they will be periodic. The dependency of the behavior on the temporal phase of the applied stress
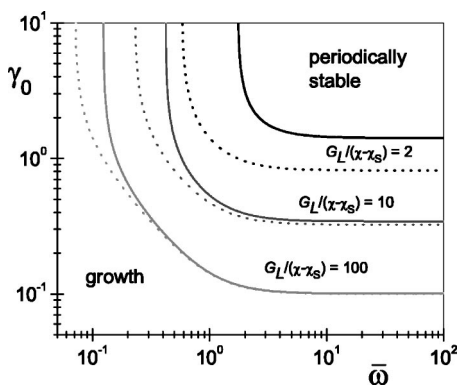
FIG. 1. Dynamic phase diagram showing the regions of suppressed growth in the flow direction in the amplitude-frequency plane of a polymer solution subjected to an oscillatory shear field. The lower and upper curves of each pair correspond to the time phases $\bar{\omega}\bar{t}_1 = \pi/2$ and $\bar{\omega}\bar{t}_1 = 0, \pi$, respectively.

arises from the oscillatory nature of the flow, which causes fluctuations with different $\bar{q}_{y0}$ values to come into the $\bar{q}_y = 0$ plane at different times. In the limit of large amplitudes, $\gamma_0 \rightarrow \infty$, the critical frequency for fluctuations in the $\bar{q}_x$ direction to stay periodically stable for *all* time phases $\bar{\omega}\bar{t}_1$ becomes

$$\bar{\omega}_c^2 = \frac{3(\chi - \chi_S)}{2\bar{G}_L - 3(\chi - \chi_S)}, \tag{11}$$

and similarly in the limit of large frequencies, $\bar{\omega} \rightarrow \infty$, the critical amplitude is

$$\gamma_{0c}^2 = \frac{2(\chi - \chi_S)}{\bar{G}_L - 3(\chi - \chi_S)}. \tag{12}$$

From Fig. 1, it can be seen that the limiting cases are reached when $\gamma_0 > O(1)$ and $\bar{\omega} > O(1)$. The dependence on the frequency is a consequence of the fact that it is the strain energy that leads to phase separation, and this increases with frequency up to $\bar{\omega} = \omega\tau_L \approx 1$, after which it remains constant. The amplitude dependence is a consequence of the magnitude of the thermodynamic term, which is coupled to the flow by convection, becoming dominated by the second term in Eq. (7).

Even when the condition of Eq. (10) is not met, the range of fluctuations that are unstable and growing is modified by the presence of the shear field. For the time phase $\bar{\omega}\bar{t}_1$, the critical wave vector representing the crossover from growth to decay of fluctuations in the flow direction is given by

$$\bar{q}_{xc}^2 = \frac{(2 + [1 + 2a]\gamma_0^2)(\chi - \chi_S) - 2\gamma_0^2 \bar{\omega}^2 \bar{G}_L/(1 + \bar{\omega}^2)}{(2 + 2[1 + 2a]\gamma_0^2 + [2a^2 + 6a + 3/4]\gamma_0^4)\bar{\kappa}}. \tag{13}$$

In Fig. 2 we show an example of the range of wave vectors that are unstable in both the flow-vorticity and the flow-gradient planes. This is simply given by the condition that Eq. (7) is zero, which leads to a quadratic dependence of $\bar{q}_x^2$ on $\bar{q}_z^2$ or $\bar{q}_y^2$. It can be seen that the temporal phase has a minimal effect on the stability condition in the flow-vorticity
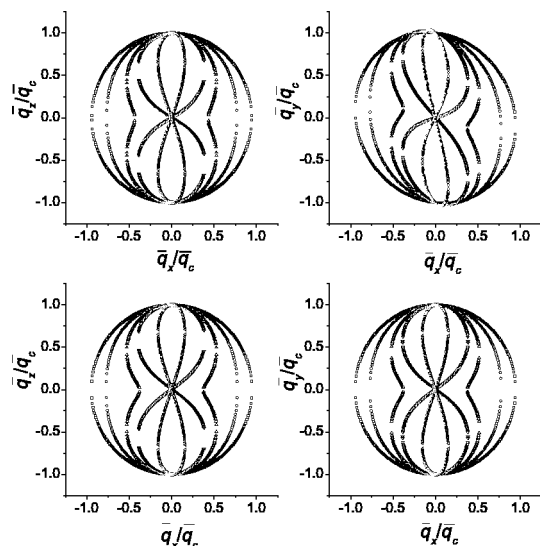

FIG. 2. Shear amplitude dependent contours on which the growth of fluctuations is zero in the flow-vorticity plane and the flow-gradient plane. Within each contour fluctuations grow. The parameters are $\bar{G}_L = 0.01$, $(\chi - \chi_S) = 0.001$, $\bar{\kappa} = 10^{-6}$, and $\bar{\omega} = 10$. From the outside contour inwards the amplitude is 0.1, 0.2, 0.3, 0.4, and 1.0. The upper two graphs correspond to the temporal phase $\bar{\omega}\bar{t}_1 = \pi/4$, and the lower two curves to the time phase $\bar{\omega}\bar{t}_1 = 0$.

plane, whereas the effect is more noticeable in the flow-gradient plane. Illustrations of the contour plots of the underlying growth rate, A_0, of fluctuations in the flow-vorticity plane are shown in Fig. 3 for $\bar{G}_L/(\chi - \chi_S) = 10$. It is clear that the fastest growing wave vector occurs when $\bar{q}_x = 0$. The values of $\bar{\omega}$ and γ_0 are chosen to represent different regions on the stability diagram (Fig. 1).

IV. PERIODIC STRUCTURE FACTORS

The corresponding values of the structure factor at wave vectors for which growth does not occur are illustrated in Fig. 4. Of particular note is the fact that, for the two instances well within the periodically stable region [Figs. 4(b) and 4(d)], the intensity maximum in the $\bar{q}_x$ direction occurs at a wave vector several times greater than the quiescent critical wave vector. This is further highlighted in Fig. 5 where we show the time dependence during one oscillatory cycle of the structure factor. The appearance of a maximum is in agreement with our predictions for the structure factor in the one-phase region of the phase diagram [16]. For completeness, we also show the structure factor for the $\bar{q}_z = 0$ plane for $\bar{\omega}\bar{t}_1 = 0$ in Fig. 6 and for $\bar{\omega}\bar{t}_1 = \pi/2$ in Fig. 7. It is worth noting that, in the case of $\bar{\omega} = 1$ and $\gamma_0 = 1$, which is shown in Figs. 6(b) and 7(b), the difference between the maximum intensity throughout the cycle is ~10 orders of magnitude. The changes throughout one cycle are shown in more detail for one example set of parameters in Fig. 8. The appearance and location of peaks in the $\bar{q}_z = 0$ plane has been observed experimentally in polymer solutions subjected to steady shear [4,5]. An explanation for enhancement of fluctuations was given by Milner [12], who argued that they
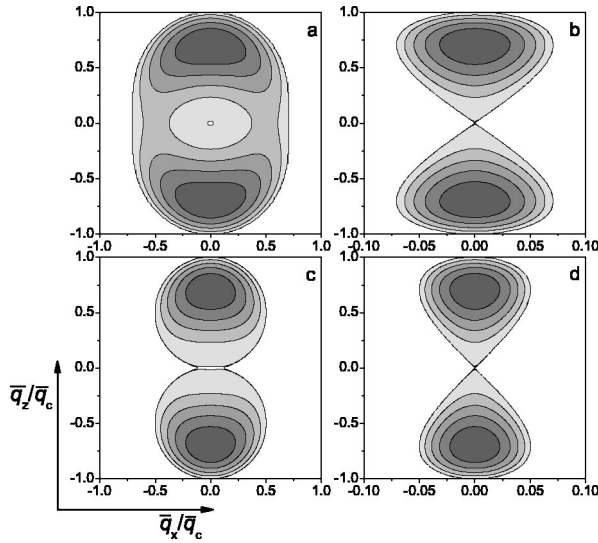
FIG. 3. Contour plots of the underlying growth rate A_0 in the flow-vorticity plane (horizontal and vertical axes, respectively) for (a) $\bar{\omega}=1$ and $\gamma_0=0.1$, (b) $\bar{\omega}=1$ and $\gamma_0=1$, (c) $\bar{\omega}=10$ and $\gamma_0=0.1$, and (d) $\bar{\omega}=10$ and $\gamma_0=1$. In each case, $\bar{G}_L=0.01$, $(\chi-\chi_S)=0.0001$, $\bar{\kappa}=10^{-6}$. The values of the contours from the outside inward are $A_0=0,-0.002,-0.004,-0.006,-0.008$. The white areas correspond to the wave vectors for which the structure factor does not grow, but remains periodic. The values of the wave vector have been divided by the quiescent critical wave vector, $\bar{q}_c = \sqrt{(\chi-\chi_S)/\bar{\kappa}}$. Note the difference in scale of the $\bar{q}_x$ axis for (c) and (d).

arise from an imbalance of elastic forces, resulting in concentrated polymer regions becoming narrower along the $\bar{q}_x=\bar{q}_y$ direction, and broader along the $\bar{q}_x=-\bar{q}_y$, when the shear flow is described by $v_x=\dot{\gamma}y$, where $\dot{\gamma}$ is the steady state shear rate. That is similar to the effect observed in Fig. 8, since during oscillatory shear the Fourier transformed flow is in
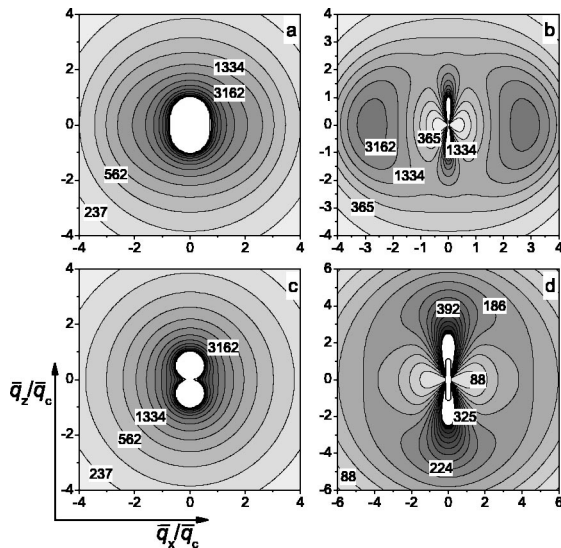

FIG. 4. Contour plots (logarithmic scale) of the structure factor corresponding exactly to the parameters used for Fig. 3, showing the intensity when $\bar{\omega}\bar{t}_1=0$. The central white areas correspond to the wave vectors for which growth occurs.
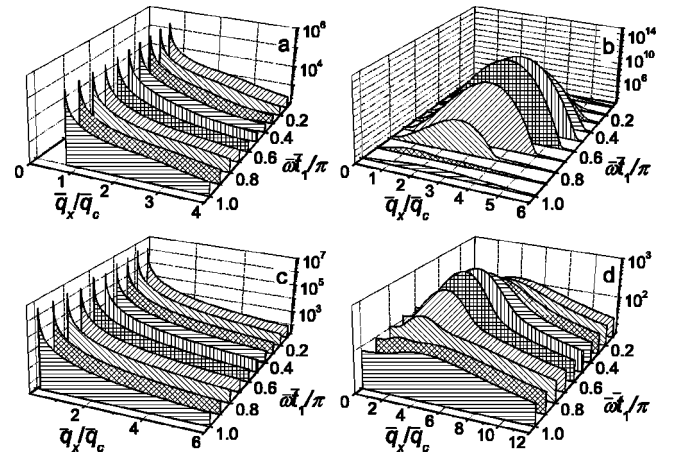

FIG. 5. Time dependence of the structure factor in the $\bar{q}_x$ direction, during a half cycle of the oscillatory shear. The parameters correspond exactly to those used for Fig. 3.

the positive $\bar{q}_x$ direction for half a cycle, and in the negative $\bar{q}_x$ direction for the other half. There is a lag between the direction of flow and the position of the peaks, which is simply a consequence of the lag between stress and strain in a viscoelastic solution. However, the patterns in the flow-gradient plane would not rotate clockwise from the $\bar{q}_y=\bar{q}_x$ line toward the direction of flow $\bar{q}_x$, as observed in steady shear [4] with the growth of shear rate $\dot{\gamma}$ ($\sim \gamma_0\bar{\omega}$ in oscillatory shear) because normal stresses are not included in our current consideration.

The large increase in the structure factor at wave vectors much greater than the critical value suggest that further understanding of the interplay between oscillatory shear and concentration fluctuations would be gained from a study beyond the linear analysis presented here. By analogy with the
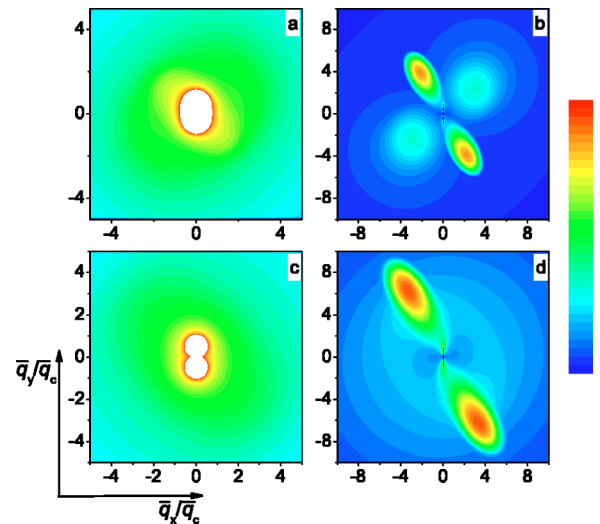

FIG. 6. (Color online) Contour plot of the structure factor in the $\bar{q}_z=0$ plane when $\bar{\omega}\bar{t}_1=0$, The parameters correspond exactly to those used for Fig. 3. The values of the wave vector have been divided by the quiescent critical wave vector $\bar{q}_c=\sqrt{(\chi-\chi_S)/\bar{\kappa}}$. The color bar scale is logarithmic, ranging from a minimum value of 10 to a maximum value of (a) 10^5, (b) 10^{16}, (c) 10^5, (d) 10^7.
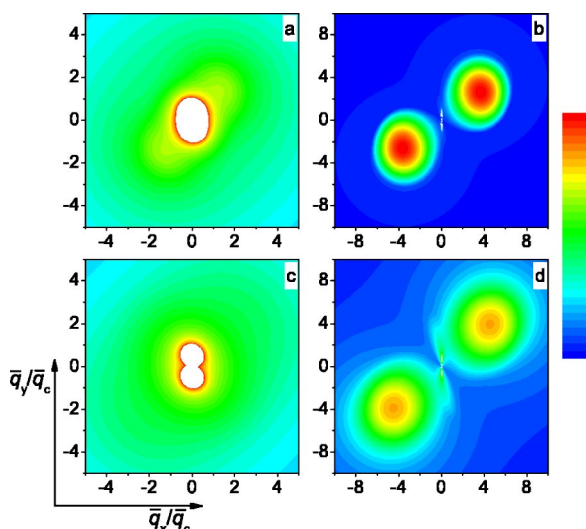
FIG. 7. (Color online) Same as Fig. 6, except $\overline{\omega}\overline{t}_1=\pi/2$. The color bar scale is logarithmic, ranging from a minimum value of 10 to a maximum value of (a) 10^5, (b) 10^{27}, (c) 10^5, (d) 10^7.

FIG. 8. (Color online) Contour plot of the structure factor in the $\overline{q}_z=0$ plane when $\overline{\omega}\overline{t}_1=0$ (a), (b) $\pi/4$, (c) $\pi/2$, (d) $3\pi/4$, (e) π, (f) $5\pi/4$, (g) $3\pi/2$, (h) $7\pi/4$, (i) 2π. The parameters correspond exactly to those used for Fig. 3(b). The values of the wave vector have been divided by the quiescent critical wave vector $\overline{q}_c=\sqrt{(\chi-\chi_S)/\overline{\kappa}}$.

behavior of large, growing, fluctuations during quiescent phase separation [24–26], in some instances the nonlinear terms may cause the peaks in the structure factor to shift to smaller values of wave vector, a consequence of the system attempting to reduce interfacial tension. However, unlike quiescent phase separation, a periodic steady state must still be reached, since, as is apparent from Figs. 4–8, at sufficiently small wave vectors the value of the structure factor decreases to such an extent that the linear theory will become valid for describing the magnitude of the fluctuations. We note that descriptions beyond the linear analysis will probably require numerical simulations of the real-space diffusion equation. The mean-field approximation [25,26], in which the probability distribution function for the concentration fluctuations is assumed to have a Gaussian form, is unlikely to be tractable when oscillatory shear stresses are included in the equation of motion for the structure factor. This serves to highlight the value of the linear analysis presented in this paper: it permits quantitative, analytical insight into the predicted phenomenon.

V. CONCLUSIONS

We have shown that shear stresses alone are sufficient to suppress phase separation in the flow direction, when oscillatory shear is applied to polymer solutions. Significantly, neither a weak nonlinear flow response due to normal forces nor a strong nonlinear flow response such as shear thinning is required, and any solution in which the viscoelastic moduli increase with the concentration of solute should display similar behavior. An experimental study probing suppression of phase separation due to temperature jump by oscillatory
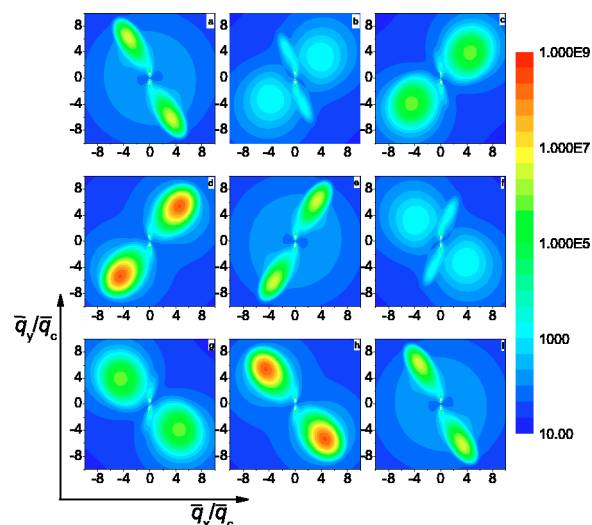
shear flow in polymer solutions would certainly be of great interest.

APPENDIX

The prefactors for the periodic contribution to the calculation of the structure factor, Eq. (6), are

$$A_1 = -8\overline{q}_{y0}\gamma_0[\overline{q}_x(\chi_S-\chi) + 2\overline{q}_0^2\overline{q}_x\overline{\kappa} + \overline{q}_x\overline{G}_L\overline{\omega}^2/(1+\overline{\omega}^2)]$$
$$- 12\overline{q}_x^3\overline{q}_{y0}\gamma_0^3\overline{\kappa}, \tag{A1}$$

$$A_2 = 4\overline{q}_x^2\gamma_0^2\overline{G}_L\overline{\omega}/(1+\overline{\omega}^2), \tag{A2}$$

$$A_3 = 4\overline{q}_{y0}\overline{q}_x^3\gamma_0^3\overline{\kappa}, \tag{A3}$$

$$B_1 = -8\overline{q}_{y0}\overline{q}_x\gamma_0\overline{G}_L\overline{\omega}/(1+\overline{\omega}^2), \tag{A4}$$

$$B_2 = 2\overline{q}_x^2\gamma_0^2[(\chi_S-\chi) + (6\overline{q}_{y0}^2 + 2\overline{q}_0^2 - \overline{q}_x^2\gamma_0^2)\overline{\kappa}$$
$$+ 2\overline{G}_L\overline{\omega}^2/(1+\overline{\omega}^2)], \tag{A5}$$

$$B_4 = \frac{1}{2}\overline{q}_x^4\gamma_0^4\overline{\kappa}. \tag{A6}$$

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