PHYSICAL REVIEW E **66**, 041802 (2002)

Effect of oscillatory shear on polymer solutions

Dmitri Miroshnychenko and Nigel Clarke
Department of Chemistry, Science Laboratories, University of Durham, South Road, Durham DH1 3LE, United Kingdom

(Received 15 January 2002; revised manuscript received 22 July 2002; published 7 October 2002)

We consider the effects of oscillatory shear flow on small concentration fluctuations in polymer solutions, which we model as highly asymmetric entangled polymer blends. A simple model that enables us to predict the scattering patterns in the flow-vorticity plane is presented. It is shown that peaks in the patterns occur in the flow direction at a finite wave vector, their position strongly depends on the angular frequency of oscillatory shear flow, whereas the intensity of these peaks is rather controlled by the amplitude of the flow. The model reproduces characteristic double-winged anisotropic scattering patterns called ‘‘butterfly,’’ which are stable and thus represent concentration fluctuations rather than phase separation.

DOI: 10.1103/PhysRevE.66.041802 PACS number(s): 61.25.Hq, 64.75.+g, 83.80.Rs, 83.80.Tc

I. INTRODUCTION

The effects of shear flows 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. The study of the response of concentration fluctuations to an external field has significantly advanced our understanding, principally because such fluctuations are quantifiable experimentally, and accessible analytically and numerically. Hence, comparison between the two enables a strong test of theoretical ideas.

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 of concentration fluctuations in polymer solutions is known to be induced by external fields, such as simple shear flows [5–8], electric fields [9], plane extensional flows [10], oscillatory shear flows [11].

From a rheological viewpoint, much of the focus has been on the effects of steady-state flows. Nevertheless, Saito *et al.* [12] have recently studied a solution of ultrahigh molecular weight polystyrene in dioctyl phthalate subjected to oscillatory shear flows using small-angle light scattering. They found that for large enough amplitudes of shear, the structures developed in the solution feature the characteristic scattering pattern in the flow-vorticity plane called ‘‘butterfly.’’

Before, butterfly patterns were reported for block copolymer films [13] stretched under uniaxial tensile stress. Lately, they have also been observed for uniaxially deformed rubbers [14,15], polymer melts [16] and swollen gels [17], and then more recently for semidilute polymer solutions under simple shear flows [4,18–21].

A number of theories have been proposed to explain butterfly patterns in stretched cross-linked polymers and swollen gels. The principal mechanism is believed to be the coupling of strain to pre-existent frozen cross-link density variations [22], the coupling of strain to polymer concentration fluctuations [23], or a combination of the two [24]. Whilst the mathematical description is rather complex, the resultant scattering pattern can effectively be considered as a sum of two Lorentzians, such that the major axis of the pattern is parallel to the direction of the stretch.

Since entanglements appear to be an important ingredient of the coupling mechanisms governing the scattering patterns in both stretched and sheared polymer systems, there are clearly some similarities in their physical behavior. However, due to the transient nature of such entanglements in sheared polymer solutions, it is the coupling between the flow field and the concentration fluctuations that will dictate the response. A significant difference is that the lobes of the butterfly patterns observed in Ref. [12] represent actual peaks in the structure factor, and hence cannot be described as the sum of two Lorentzians.

Theoretical efforts to understand this complex behavior are primarily concerned with developing a framework that couples the effects of external fields in polymer systems with the presence of concentration fluctuations. Current progress and new theoretical challenges in the dynamics of complex fluids are broadly summarized in the proceedings volume [25].

Different ideas explaining the effect of shear flow on polymer solutions and blends have been proposed [26]. Some models [27] start by adding a shear rate dependent elastic energy term to the Flory-Huggins free energy to form thus the total free energy of a polymer solution. These considerations lead to a thermodynamical theory of shear-induced phase separation, which, however, has not yet been used to predict scattering patterns.

The latter can be obtained through the dynamical approach, which incorporates the mechanism of coupling between stress and diffusion into the dynamics of concentration fluctuations [28,29]. A time-dependent Ginzburg–Landau scheme [30–33] introduces a conformation tensor, corresponding to chain deformations in viscoelastic fluids, as a new independent dynamical variable of the free energy.

We note that the mechanism of dipolar coupling between concentration fluctuations and an electric field in polymer solutions has been proposed [34] as well. The shift in spinodal curve induced by an electric field, which suppresses phase separation in polymer solutions, has also been considered [35].

Yet oscillatory shear flows have received relatively little attention theoretically. Malevanets and Yeomans [36] 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. [12]; however, direct comparison is not possible since the experiments and numerical calculations were carried out in different planes with respect to the flow direction.

In this paper we develop an analytical theory to predict the structure factor arising from small concentration fluctuations in polymer solutions under oscillatory shear. This simple model may be easily used to calculate scattering from both the flow-shear gradient and the flow-vorticity planes, and we show that it may explain some of the underlying features observed in Ref. [12].

We utilize the approach of Doi and Onuki [29], 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 or blend 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. [29] it was assumed that the response of individual polymers to shear flow could be described by a single relaxation time. The model was recently modified to account for the rheological response of a binary blend in which each component has distinctly different relaxation times [37–39]. This approach gives rise to an explicit concentration dependence of the components of the stress tensor, the advantage of which, even for a system in which the stress relaxation can be described by one dominant time scale, is illustrated below.

II. CONCENTRATION FLUCTUATIONS

A. Linearised equation

The shear strain in oscillatory shear flow is described by $\gamma(t)=\gamma_0 \sin(\omega t)$, so that the velocity profile is $v_x=\gamma_0\omega \cos(\omega t)y$, where x denotes the flow direction and y denotes the shear gradient direction, γ_0 is the amplitude of the flow, and ω is its angular frequency. We consider the effect that such a flow has on a polymer blend, in which one component has a much greater molecular weight than the other, and is consequently much more entangled. We denote the volume fraction of the higher molecular weight polymer ϕ_{L}, and we assume incompressibility, such that $\phi_{\mathrm{L}}+\phi_{\mathrm{S}}=1$, where ϕ_{S} is the volume fraction of the lower molecular weight polymer.

Since we shall only be interested in how flow affects the small fluctuations, it is sufficient to study the linearised equation of motion for a fluctuation in $\mathbf{q}$ space, $\delta\phi_{\mathrm{L}}(\mathbf{q},t)$. If we assume that $N_{\mathrm{L}}\gg N_{\mathrm{S}}$, where N_i is the degree of polymerization of component i, then we have [29]

$$\frac{\partial \delta\phi_{\mathrm{L}}(\mathbf{q},t)}{\partial t}=\theta(\mathbf{q},t)+\dot{\gamma} q_x \frac{\partial \delta\phi_{\mathrm{L}}(\mathbf{q},t)}{\partial q_y}-M\left[2q^2(\chi_{\mathrm{S}}-\chi+\kappa q^2)-\frac{q_i q_j}{k_{\mathrm{B}}T\langle\phi_{\mathrm{L}}\rangle}\frac{\delta\sigma_{ij}^{(\mathrm{n})}}{\delta\phi_{\mathrm{L}}}\right]\delta\phi_{\mathrm{L}}(\mathbf{q},t), \qquad (1)$$

where M is the mobility, κ is the interfacial energy, χ is the Flory-Huggins interaction parameter and χ_{S} is its value on the quiescent spinodal, $\sigma_{ij}^{(\mathrm{n})}$ 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,

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

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

The second term on the right hand side in Eq. (1) represents the convective effect of shear. This has important consequences in steady-state shear flows: if a fluctuation with a component in the q_x direction becomes unstable due to the flow, it will be convected to wave vectors with larger values of the q_y component, and eventually become stable again [32]. However, in oscillatory shear flows the q_y value of a fluctuation, with nonzero q_x, varies sinusoidally. This immediately raises the possibility of unusual phenomena, since unstable fluctuations are not convected away.

B. Stress tensor

In this paper we shall consider only the effects that the shear stress component $\sigma_{xy}^{(\mathrm{n})}$ of the stress tensor has on the fluctuations and neglect the consequences that arise due to normal stress differences, which have been explored analytically by Helfand and Fredrickson [28] and then numerically [33]. One consequence of this simplification is that spatial variations of the flow field are not important [32].

In order to model the shear stress of an entangled polymer blend, we use a modified version of the reptation model, in which the effect of surrounding polymers on the dynamics of any given polymer is replaced by an effective tube [40]. The polymer is free to diffuse along the tube, but motion lateral to it is restricted. In the original version of the model [41], stress is directly related to the amount of a polymer that has not escaped from the tube surrounding it at the time of the application of the strain.

Following our recent work [37,39] on the effects of steady-state flow on phase separation in polymer blends, we model the molecular response of the solution to shear flow, represented by the stress relaxation function, $G(t-t')$, using the idea of double reptation due to des Cloiseaux [42] and Tsenoglou [43]. Double reptation accounts, in the simplest possible way, for the fact that polymers do not reptate in fixed tubes, as assumed in the original reptation model. The surrounding polymers, which form the tube, also relax, and so the constraints that form the tube decay with a characteristic time scale. In other words, stress relaxation depends not only on the dynamics of each individual polymer, but also on the dynamics of the surrounding polymers.

A particular appeal of the double reptation model is the simple relation between the stress relaxation function of the blend and the Doi-Edwards stress relaxation function for polymers in a fixed network, $F_{\mathrm{p}}(t)$. For a highly asymmetric blend only the high molecular weight component contributes significantly to the stress, hence we can approximate the

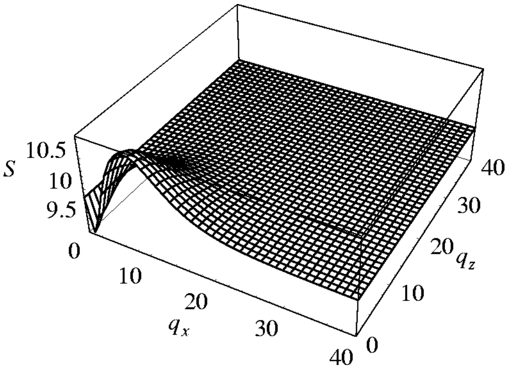

FIG. 1. The scattering function calculated in the flow-vorticity plane at fixed $\overline{\omega}=10.0$ for $\gamma_0=2.2$.

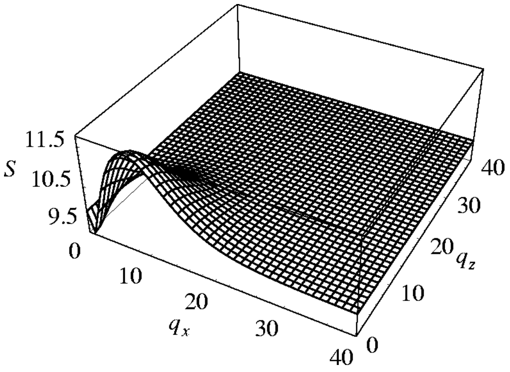

FIG. 2. The scattering function calculated in the flow-vorticity plane at fixed $\overline{\omega}=10.0$ for $\gamma_0=3.2$.

stress relaxation function according to the double reptation model as

$$G(t)=\phi_{\mathrm{L}}^2 G_{\mathrm{L}} F_{\mathrm{p}}(t), \tag{2}$$

where G_{L} is the plateau modulus of the high molecular weight polymer. $F_{\mathrm{p}}(t)$ physically corresponds to the probability of tube survival in a matrix of identical relaxing obstacles. As was shown by Doi and Edwards [41], the probability of tube survival in a matrix of fixed obstacles is almost single exponential; hence, the dynamics are dominated by a single time scale, the terminal relaxation time. Consequently, we have [44]

$$G(t)=\phi_{\mathrm{L}}^2 G_{\mathrm{L}} e^{-t/\tau_{\mathrm{L}}}, \tag{3}$$

where τ_{L} represents some relaxation time which, in terms of the tube model, is related to the idealised Doi-Edwards relaxation time $\tau_{\mathrm{L}}^{(\mathrm{DE})}$ for the polymer in a matrix of fixed obstacles by $\tau_{\mathrm{L}}=(1/2)\tau_{\mathrm{L}}^{(\mathrm{DE})}$.

The principle advantage of this model is that the dependence of the stress relaxation modulus on the concentration is explicit; we assume that there is no dependence of the relaxation time and the plateau modulus on concentration. This enables us to decouple the equations of motion for the concentration fluctuations and for the stress; thus simplifying our efforts to solve the problem.

The simplest constitutive equation relating the stress relaxation modulus to the shear stress is given by the Maxwell model [45]

$$\sigma_{xy}^{(\mathrm{n})}(t)=\int_{-\infty}^{t}\frac{\partial G(t-t')}{\partial t'}[\gamma(t)-\gamma(t')]dt'. \tag{4}$$

In oscillatory shear flows, Eqs. (3) and (4) lead to an expression for the shear stress in adiabatic approximation

$$\sigma_{xy}^{(\mathrm{n})}(t)=\frac{\phi_{\mathrm{L}}^2 G_{\mathrm{L}}\gamma_0}{1+\omega^2\tau_{\mathrm{L}}^2}[\omega^2\tau_{\mathrm{L}}^2\sin(\omega t)+\omega\tau_{\mathrm{L}}\cos(\omega t)], \tag{5}$$

which is a simple function of concentration.

C. Structure factor

Inserting Eq. (5) into Eq. (1) we arrive at the desired equation of motion for a concentration fluctuation. This can be converted using the method of characteristics into an equation of motion for the structure factor, $S(\overline{\mathbf{q}},\overline{t})=\langle|\delta\phi_{\mathrm{L}}(\overline{\mathbf{q}},\overline{t})|^2\rangle$, in terms of reduced variables, $\overline{q}^2=q^2M\tau_{\mathrm{L}}$, $\overline{t}=t/\tau_{\mathrm{L}}$, $\overline{\omega}=\omega\tau_{\mathrm{L}}$, $\overline{G}_{\mathrm{L}}=G_{\mathrm{L}}/k_{\mathrm{B}}T$, and $\overline{\kappa}=\kappa/M\tau_{\mathrm{L}}$,

$$\frac{dS}{d\overline{t}}=D(\overline{\mathbf{q}},\overline{t})S+C(\overline{\mathbf{q}},\overline{t})=-\Bigg\{4\overline{q}^2(\chi_{\mathrm{S}}-\chi+\overline{\kappa}\overline{q}^2)-\frac{8\overline{q}_x\overline{q}_y\overline{G}_{\mathrm{L}}\gamma_0}{1+\overline{\omega}^2}[\overline{\omega}^2\sin(\overline{\omega}\overline{t})+\overline{\omega}\cos(\overline{\omega}\overline{t})]\Bigg\}S+2\overline{q}^2. \tag{6}$$

The consequence of the oscillatory convection term in Eq. (1) is that the component of the wave vector in the shear gradient direction is not constant, and is described by $\overline{q}_y=\overline{q}_{y0}-\gamma_0\overline{q}_x\sin(\overline{\omega t})$. This expression is substituted into Eq. (6), which may then be solved for given values of $\overline{q}_x$, $\overline{q}_z$, and $\overline{q}_{y0}$; the solution yields the structure factor for $\overline{q}_x$, $\overline{q}_z$, and $\overline{q}_y$, where the value of the latter depends on the phase $\overline{\omega t}$.

The scattering function can be found from Eq. (6), which is a first-order nonhomogeneous linear differential equation, through the method of integrating factor,

$$S(\overline{\mathbf{q}},\overline{t})=S_0(\overline{\mathbf{q}}_0)\cdot\exp\left(\int_0^{\overline{t}}D(\overline{\mathbf{q}},t')dt'\right)+\int_0^{\overline{t}}C(\overline{\mathbf{q}},\overline{t})\times\exp\left(-\int D(\overline{\mathbf{q}},t')dt'\right)dt'\cdot\exp\left(\int D(\overline{\mathbf{q}},\overline{t})d\overline{t}\right), \tag{7}$$

where the structure factor at time $\overline{t}=0$ is defined as

$$S(\overline{\mathbf{q}},\overline{t}=0)\equiv S_0(\overline{\mathbf{q}}_0)=\frac{1}{2[\chi_{\mathrm{S}}-\chi+\overline{\kappa}(\overline{q}_x^2+\overline{q}_{y0}^2+\overline{q}_z^2)]}.$$

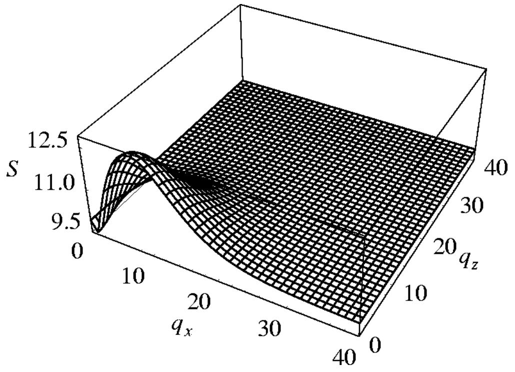

FIG. 3. The scattering function calculated in the flow-vorticity plane at fixed $\bar{\omega}=10.0$ for $\gamma_0=4.2$.

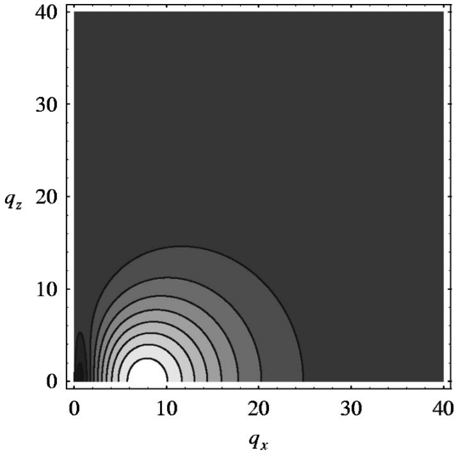

FIG. 5. The contour plot for concentration fluctuations calculated in the flow-vorticity plane at fixed $\gamma_0=4.2$ for $\bar{\omega}=10.0$.

III. SCATTERING PATTERNS

A. Parameters

The mobility for an asymmetric polymer blend has been shown [46] to have the form $M\approx k_{\mathrm{B}}T\langle\phi_{\mathrm{L}}\rangle^2\langle\phi_{\mathrm{S}}\rangle^2/\zeta_0$, where ζ_0 is the monomeric friction coefficient, which for simplicity we assume it to be equal for both components. According to the tube model the relaxation time of the high molecular weight polymer in a fixed matrix is given by $\tau_{\mathrm{L}}\approx N_{\mathrm{L}}^3b^2\zeta_0/k_{\mathrm{B}}T\pi^2N_{\mathrm{e}}$. Hence, we have $M\tau_{\mathrm{L}}\approx\langle\phi_{\mathrm{L}}\rangle^2\langle\phi_{\mathrm{S}}\rangle^2N_{\mathrm{L}}^3b^2/\pi^2N_{\mathrm{e}}$. This gives the formula for the reduced value of κ as $\bar{\kappa}\approx\pi^2N_{\mathrm{e}}/36\langle\phi_{\mathrm{L}}\rangle^3\langle\phi_{\mathrm{S}}\rangle^3N_{\mathrm{L}}^3$. The plateau modulus per monomer volume is directly related to the degree of polymerization between entanglements, N_{e}, by $\bar{G}_{\mathrm{L}}\approx 1/N_{\mathrm{e}}$. The critical value of χ parameter on the quiescent spinodal is given by $2\chi_{\mathrm{S}}=1/N_{\mathrm{L}}\langle\phi_{\mathrm{L}}\rangle+1/(1-\langle\phi_{\mathrm{L}}\rangle)$.

Consequently, for a strongly asymmetric blend, the problem is completely defined by the parameters, N_{L}, N_{e}, $\langle\phi_{\mathrm{L}}\rangle$, and χ. Although the theory of Doi and Onuki is strictly applicable to entangled polymer blends only, we have solved Eq. (6) using realistic parameters that conform as closely as possible to the polystyrene solution studied experimentally by Saito *et al.* [12], i.e., $N_{\mathrm{L}}=52\,692$, $N_{\mathrm{e}}=174$, $\langle\phi_{\mathrm{L}}\rangle=0.06$, and $\chi=0.4813$. The window 3.96×10^{-4} nm^{-1} $\leqslant q_x\leqslant 3.43\times10^{-3}$ nm^{-1} observed in the experiments [12] corresponds to the range of reduced units $4.4\leqslant\bar{q}_x\leqslant37.8$ given by $\bar{q}_x=q_x(11.0\times10^3)$ nm. The length of the bond in the lattice is taken to be $b=6.7$ Å.

B. Results and discussion

Since the flow-vorticity plane $\bar{q}_y=0$ is the most experimentally accessible, we have calculated the scattering patterns in it (Figs. 1–6) at the moment $\bar{t}=\bar{t}_1$ with $\bar{q}_{y0}=\gamma_0\bar{q}_x\sin(\overline{\omega t}_1)$. It should be noted that even in flow-vorticity plane, the effects of the shear flow are important since fluctuations with nonzero values of $\bar{q}_y$ are continuously convected into and out of the $\bar{q}_y=0$ plane.

The results presented in this paper have been calculated for the phase $\overline{\omega t}_1=\pi/2+2\pi n(n\in\mathbb{N}\cup\{0\})$, when the scattering intensity is the strongest. We show the structure factor after one hundred cycles ($n=100$) of the strain, although all

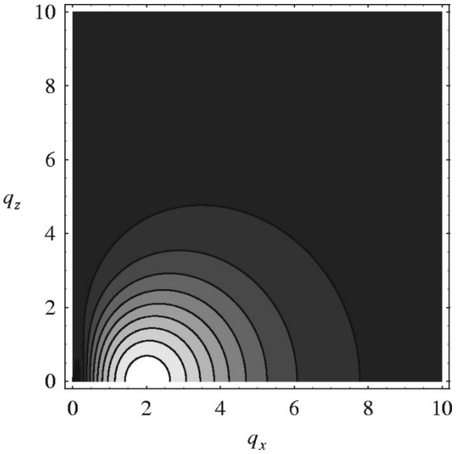

FIG. 4. The contour plot for concentration fluctuations calculated in the flow-vorticity plane at fixed $\gamma_0=4.2$ for $\bar{\omega}=1.0$.

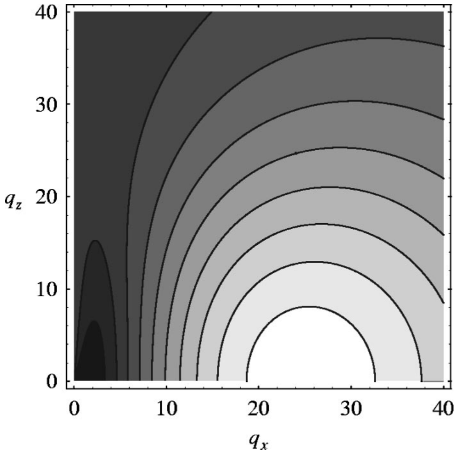

FIG. 6. The contour plot for concentration fluctuations calculated in the flow-vorticity plane at fixed $\gamma_0=4.2$ for $\bar{\omega}=100.0$.

become cyclically stable after just one cycle. It can be seen that the peaks in the patterns occur in the flow direction at a finite $\overline{q}_x = \overline{q}_{x\max}$.

Figures 1–3 with fixed $\overline{\omega}$ show that as γ_0 is increased the peaks in the flow direction become more pronounced, although the position $\overline{q}_{x\max}$ of the peak is shifted just slightly towards higher value of $\overline{q}_x$. When the amplitude γ_0 is fixed (Figs. 4–6), the value of the structure factor in the peak is almost unaltered by increasing $\overline{\omega}$, although there is a tendency to slightly decrease, whereas the position $\overline{q}_{x\max}$ of the peak shifts towards higher $\overline{q}_x$ region significantly.

IV. CONCLUSIONS

Our results are in excellent qualitative agreement with the experimental work of Saito *et al.* [12]. The model reproduces double-winged anisotropic behavior with characteristic scattering patterns called ‘‘butterfly.’’ The position of the peak strongly depends on the angular frequency of oscillatory shear, whereas the intensity of these peaks is rather controlled by the amplitude of the flow.

The scattering patterns we predict are stable and thus represent concentration fluctuations rather than phase separation.

[1] M.L. Fernandez, J.S. Higgins, and S.M. Richardson, Trans. Inst. Chem. Eng., Part A **71**, 239 (1993).
[2] M.L. Fernandez, J.S. Higgins, R. Horst, and B.A. Wolf, Polymer **36**, 149 (1995).
[3] H. Gerard, J.S. Higgins, and N. Clarke, Macromolecules **32**, 5411 (1999).
[4] X.-L. Wu, D.J. Pine, and P.K. Dixon, Phys. Rev. Lett. **66**, 2408 (1991).
[5] T. Hashimoto and K. Fujioka, J. Phys. Soc. Jpn. **60**, 356 (1991).
[6] P.K. Dixon, D.J. Pine, and X.-L. Wu, Phys. Rev. Lett. **68**, 2239 (1992).
[7] P. Yanase, Moldenaers, J. Mewis, V. Abetz, J.W. van Egmond, and G.G. Fuller, Rheol. Acta **30**, 1 (1991); P. Moldenaers, H. Yanase, J. Mewis, G.G. Fuller, C.S. Lee, and J.J. Magda, *ibid.* **32**, 1 (1993).
[8] B. Hammouda, A.I. Nakatani, D.A. Waldow, and C.C. Han, Macromolecules **25**, 2903 (1992); A.I. Nakatani, J.F. Duglas, Y.-B. Ban, and C.C. Han, J. Chem. Phys. **100**, 3224 (1994).
[9] D. Wirtz, K. Berend, and G.G. Fuller, Macromolecules **25**, 7234 (1992); D. Wirtz, and G.G. Fuller, Phys. Rev. Lett. **71**, 2236 (1993).
[10] J.W. van Egmond and G.G. Fuller, Macromolecules **26**, 7182 (1993).
[11] J. Lai and G.G. Fuller, J. Rheol. **39**, 893 (1995); **40**, 153 (1996).
[12] S. Saito, K. Matsuzaka, and T. Hashimoto, Macromolecules **32**, 4879 (1999).
[13] T. Inoue, M. Moritani, T. Hashimoto, and H. Kawai, Macromolecules **4**, 7182 (1971).
[14] *Polymer Motion in Dense Systems*, edited by D. Richter and T. Springer, (Springer, Berlin, 1988).
[15] R. Oeser, C. Picot, and J. Herz, in *Polymer Motion in Dense Systems*, Ref. [14], p. 104.
[16] J. L. Barea, R. Muller, and C. Picot, in *Polymer Motion in Dense Systems*, Ref. [14], p. 86; J. Bastide, M. Buzier, and F. Boué, Ref. [[14]], p. 112.
[17] J. Bastide, L. Leiber, and J. Prost, Macromolecules **23**, 1821 (1990); E. Mendes, P. Lindner, M. Buzier, F. Boué, and J. Bastide, Phys. Rev. Lett. **66**, 1595 (1991).
[18] T. Hashimoto and T. Kume, J. Phys. Soc. Jpn. **61**, 1839 (1992); E. Moses, T. Kume, and T. Hashimoto, Phys. Rev. Lett. **72**, 2037 (1994).
[19] J.W. van Egmond, D.E. Werner, and G.G. Fuller, J. Chem. Phys. **96**, 7742 (1992).
[20] F. Boué and P. Lindner, Europhys. Lett. **25**, 421 (1994).
[21] K. Migler, C.H. Liu, and D.J. Pine, Macromolecules **29**, 1422 (1996).
[22] J. Bastide and L. Leibler, Macromolecules **21**, 2647 (1988).
[23] Y. Rabin and R. Bruinsma, Europhys. Lett. **20**, 79 (1992).
[24] A. Onuki, J. Phys. Soc. Jpn. **58**, 3065 (1989).
[25] *Theoretical Challengers in the Dynamics of Complex Fluids*, edited by T. McLeish, (Kluwer Academic, Dordrecht, 1997).
[26] A. Onuki, J. Phys.: Condens. Matter **9**, 6119 (1997).
[27] C.F. Rangel-Nafaille, A.B. Metzner, and K.F. Wissburn, Macromolecules **17**, 1187 (1984); R. Horst and B.A. Wolf, *ibid.* **26**, 5676 (1993); D. Jou, J. Casas-Vázquez, and M. Criado-Sancho, Adv. Polym. Sci. **120**, 207 (1995).
[28] E. Helfand and G.H. Fredrickson, Phys. Rev. Lett. **62**, 2468 (1989).
[29] M. Doi and A. Onuki, J. Phys. II **2**, 1631 (1992).
[30] A. Onuki, Phys. Rev. Lett. **62**, 2472 (1989); J. Phys. Soc. Jpn. **59**, 3423 (1990); **59**, 3427 (1990).
[31] S.T. Milner, Phys. Rev. Lett. **66**, 1477 (1991).
[32] S.T. Milner, Phys. Rev. E **48**, 3674 (1993).
[33] H. Ji and E. Helfand, Macromolecules **28**, 3869 (1995).
[34] D. Wirtz, D.E. Werner, and G.G. Fuller, J. Chem. Phys. **101**, 1679 (1994).
[35] E. Gurovich, Macromolecules **28**, 6078 (1995).
[36] A. Malevanets and J. Yeomans, Faraday Discuss. **112**, 237 (1999).
[37] N. Clarke and T.C.B. McLeish, Phys. Rev. E **57**, R3731 (1998).
[38] N. Clarke and T.C.B. McLeish, Macromolecules **32**, 4447 (1999).
[39] N. Clarke, Faraday Discuss. **112**, 249 (1999).
[40] P.-G. de Gennes, J. Chem. Phys. **55**, 572 (1971).
[41] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Oxford University Press, Oxford, 1986).
[42] J. des Cloiseaux, Europhys. Lett. **5**, 437 (1988).
[43] C. Tsenoglou, Macromolecules **24**, 1762 (1991).
[44] D.W. Mead, J. Rheol. **40**, 633 (1996).
[45] R. G. Larson, *Constitutive Equations for Polymer Melts and Solutions* (Butterworths, Boston, 1988).
[46] E.J. Kramer, P. Green, and C.J. Palmstrøm, Polymer **25**, 473 (1984).