Dynamics and flow-induced phase separation in polymeric fluids

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The past few years have seen many advances in our understanding of the dynamics of polymeric fluids. These include improvements on the successful reptation theory; an emerging molecular theory of semiflexible chain dynamics; and an understanding of how to calculate and classify “phase diagrams” for flow-induced transitions. Experimentalists have begun mapping out the phase behavior of wormlike micelles, a “living” polymeric system, in flow: these systems undergo transitions into shear-thinning or shear-thickening phases, whose variety is remarkably rich and poorly understood. Polymeric ideas must be extended to include the delicate charge and composition effects which conspire to stabilize the micelles and are strongly influenced by flow.

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1 Introduction

The field of non-linear rheology is roughly fifty years old and far from mature. Non-linear fluids often display elastic effects, and have effective viscosities which depend on stress or strain rate. Polymeric liquids typically shear-thin [1], although branched polymers thicken dramatically in extensional flow; colloidal suspensions of platelike particles (clays) typically shear-thicken; and solutions of surfactant (soap) molecules can shear-thicken or shear-thin.

Non-linear rheology and polymer dynamics are immense fields, and in this short (subjective) review I will focus on a few subfields. I will discuss recent advances in modelling the dynamics of flexible and semiflexible polymer melts, including linear and complex topologies; and then review progress in our knowledge of the surfactant wormlike micelle system, to which concepts from polymer dynamics have been successfully applied. Unlike conventional polymers, the micellar microstructure can change qualitatively in flow conditions; these transitions have many features in common with equilibrium phase transitions, and have excited great interest. A good collection of results from a wide range of complex fluids may found in [2].

2 Polymer Melts and Solutions

The most accepted molecular model for the dynamics of flexible entangled polymers has been the Doi-Edwards (DE) theory, based on de Gennes’ reptation concept, in which polymers are envisaged to occupy “tubes” that model entanglement constraints. This has done a reasonable job in predicting linear rheology, with a few notable exceptions such as the failure to predict the scaling of the zero frequency viscosity as \( M^{3.4} \), although recent work suggests that contour length [3] fluctuations are a key to this puzzle.

Recent work in the linear regime includes applying the tube picture to molecules with complex branched topologies [4]. Star polymers afford stringent tests of tube model ideas, because diffusion is dominated by arm retraction in its tube, which is exponential in the retraction potential. Inclusion of higher-order Rouse modes along with “dynamic dilution” of the tube has led to remarkably good agreement with experiment [5]. In addition to star polymers, molecular models have recently been developed for progressively more complex topologies, paving the way for understanding the flow behavior of industrially-important long-chain-branched polymers, which strain-harden in extensional flow while softening in shear flow [4].

Although the DE tube picture works well in the linear regime, it has several defects at high strain rates, particularly in steady shear. For example: experiments show a slightly increasing plateau shear and an increasing normal stress for strain rates \( \gamma \) above an inverse reptation time \( \tau_{r}^{-1} \), while theory predicts a decreasing stress \( \sigma \sim \gamma^{-1} \) and a constant normal stress; and the DE theory predicts a high strain rate viscosity which decreases with molecular weight, while experiments merge onto a molecular weight-independent curve. The defect in DE theory is that, as the tube representing entanglement constraints rotates into the flow, the entrapped polymer feels a reduced stress and, at strain rates above the inverse tube relaxation time \( \tau_{r}^{-1} \), remains oriented and presents a decreasing stress with increasing strain rate. Although corrections due to tube stretching [6] have accounted for some problems in startup flows, this only applies near \( \gamma \sim \tau_{r}^{-1} \) and still predicts a pronounced stress maximum. Another mechanism is needed to relax the chain and hence increase the stress by providing more misaligned material for the flow to “grip”. The key is believed to lie in “convected constraint release”, whereby the entanglement (tube) mesh convects away at high strain rates, leaving a relaxed coil. Early applications of this idea [7,8] have cleared up several problems with the DE theory, although the theory still predicts a slightly decreasing stress with strain rate, so it should be regarded as provisional.

While moderately successful molecular theories of flexible polymer and rigid rod dynamics have existed since the ‘70’s, the study of semiflexible polymers (in which \( d < L_{p} < L \)), where \( d \) is the polymer diameter, \( L_{p} \) the persistence length, and \( L \) the length) is quite young, mainly due to the severe mathematical difficulties in treating the bend degrees of freedom and length constraint. However, with increasing attention being paid to biological polymers such as actin [9], a deeper understanding of the dynamics of semiflexible polymer solutions is emerging. Direct imaging of tagged fluorescent polymers is possible [10], and several techniques have been developed for measuring elastic moduli, including direct (torsional oscillator [11]) and indirect (from various optical techniques [12,13]). Experiments indicate the vestiges of a plateau modulus, less pronounced than that of flexible polymer solutions. For polymers with \( L_{p} < L_{c} \), the distance between entanglements or confinement constraints (or deflection length [4]), one expects the behavior of flexi-
ble solutions. However, for \( L_p > L_e \) one expects qualitatively different effects due to the perturbation of bending modes by tube constraints. While Odijk and Semenov [14, 15] have studied the dynamics and statistics of individual filaments, only recently have molecular theories for the stress response of entangled solutions emerged. Unlike flexible polymers, semiflexible chains have a bending energy which maintains \( L_p \), and one can distinguish between longitudinal and transverse conformational changes. Two pictures have emerged for the origin of elastic stress in concentrated solutions: Isambert and Maggs [16] argued that semiflexible chains can slide along their tubes longitudinally, and relaxation only occurs when transverse motions allow escape from the tubes. MacKintosh et al. [17] argued that, if longitudinal motion is suppressed, then the modulus is due to the applied tension and the relaxation of bending modes (which are present in the quiescent state due to thermal fluctuations). In the case of solutions the former mechanism is expected to hold at times longer than that on which chain tension can relax [18]. These pictures have been made more quantitative by Morse [19], who has developed a molecular theory at the level of the Doi-Edwards theory and included the bending curvature explicitly in the expression for the microscopic stress tensor.

3 Flow instabilities in Wormlike Micelles

DE theory predicts a bulk flow instability in polymer melts which has not been seen; however, a suggestive instability known as the "spurt effect" has been seen in extrusion, in which the throughput increases dramatically above a critical pressure gradient, often accompanied by a spatial pattern in the extrudate [20, 21]. Current opinion is that this is a surface instability, although the picture is not settled [22]. However, there is a polymeric system which displays a well-documented bulk instability and has been the subject of intense investigation in the past decade.

Certain aqueous surfactant solutions (e.g. cetylpyridinium chloride/sodium salicylate [CPCI/NaSal]; cetyltrimethylammonium bromide(CTAB)/NaSal) self-assemble into flexible cylindrical micelles with an annealed length distribution that can encompass polymeric dimensions (microns). These solutions comprise a surfactant (e.g. CPCI) and an ionizing salt (e.g. NaSal) which together determine micellar dimensions, flexibility, and interactions. Salt and concentration effects are quite delicate, with Coulomb interactions playing an important and poorly-understood role. Micelle reaction kinetics introduce additional timescales to the Rouse and reptation times of conventional polymers: in the limit of fast breaking times the stress relaxation of entangled micelles often obeys a simple single exponential ("Maxwell fluid"), and properties can be calculated quite confidently [23, 24], in good agreement with experiment [25]. Some non-linear properties can be calculated in this limit, and a maximum in the shear stress (analogous the stress maximum in DE theory) is predicted at an inverse relaxation time \( \gamma_p \) (predicted by Cates [26] for semi-dilute systems), while the composite steady state flow curve has a plateau beginning at \( \sigma_p < \sigma_{max} \). [It is important to note that micellar systems have slow dynamics, and one can trap metastable states for \( \sigma > \sigma_p \) [27].] This occurs in semi-dilute systems, of order a few percent surfactant [28], or in more concentrated systems (order 30%) with a nearby equilibrium nematic transition [29, 30]. In the former case the dynamic instability is believed to be poly-

![Figure 1: Model constitutive relation \( \sigma(\gamma) \) for a shear-thinning complex fluid with a bulk instability (after Ref. [29]). The thick curve shows the kind of curve envisioned for wormlike micellar solutions: this one is from the Johnson-Segalman model [54]. Portions of the curve with negative slope are mechanically unstable. Both the Doi-Edwards theory for polymer melts and the Cates theory for micelles predict a constitutive curve qualitatively like the thin curve, with a continuously decreasing stress above a critical strain rate \( \gamma_c \). Convected constraint release [32] has reduced the instability in the polymer melt theory to a slight bump, while micellar theories still rely on an implicit solvent viscosity to stabilize the high strain rate branch (if there is indeed one). The portion of the curve with negative slope is unstable. Experiments show that, for applied strain rates \( \gamma > \gamma_p \), micellar solutions can phase separate under shear, attaining a unique steady state stress \( \sigma_p(\gamma) \) in both phases, with a portion of the sample at a high shear rate \( \gamma_2 \) and a portion at the low shear rate \( \gamma_1 \approx \gamma_p \). A dependence of \( \sigma_p \) on \( \gamma \) (not in this case) implies different compositions in the coexisting phases, so that different constitutive curves are connected; and all properties change with mean strain rate [33].]
meric in nature \[\{26\}\], while the latter may be due to nematic effects (probably both effects are present). No theories exist for nematic transitions under shear in micelles, although recent work includes phase diagrams for model rigid-rod suspensions in shear flow \[\{32\}\], for which only a few results exist \[Ref. \{53\}\ reported a shear-induced nematic transition in a liquid crystal polymer melt\].

Shear banding can be inferred from rheological measurements and directly observed optically. Quantitative measurements include the fraction of material and degree of alignment in the two phases, inferred from neutron scattering \[\{34\}\]; and the velocity profile, measured directly using magnetic resonance imaging \[\{35\}\]. Shear-banding can incorporate different concentrations in the two phases, which is expected when flow modifies intermicellar interactions (as near a nematic transition) rather than simply the micellar conformation (as might be expected in more dilute systems). A signature of this is a slope in the “plateau” stress with increasing mean strain rate \[\{36\}\, \{33\}\], indeed seen in concentrated solutions which often have an underlying nematic transition \[\{7\}\, \{5\}\, \{59\}\, \{34\]\.

Groups have begun investigating metastability. Berret et al. \[\{49\}\, \{7\}\] examined slow transients in 10-20% CPCl/NaSal solutions. After increasing the strain rate into the two-phase region the stress decayed slowly in time from the underlying constitutive curve onto the stress plateau, with behavior \(\sigma \sim \exp \left\{-\left(t/\tau(\gamma)\right)^{\alpha}\right\}\), \(\alpha = 2\), which they interpreted as one-dimensional nucleation and growth. Grand et al. \[\{42\}\] studied transients in more dilute (\(~1\)%) CPCl/NaSal solutions and found similar stress decays, with \(\alpha \simeq (2, 2.5, 3)\), and \(\tau(\gamma)\) diverging above or below (depending on composition) the strain rate \(\gamma_p\) at the onset of banding. They also performed controlled stress experiments, and discovered a stress \(\sigma_{\text{jump}} > \sigma_p\), below which the system remained on the low strain rate branch indefinitely and above which the system eventually jumped to the high strain rate branch. Their data suggested that some compositions behave “spinodal-like” and others behave “nucleation-like” (as Berret’s did), but it is to early to completely embrace the language of first-order transitions \((\text{given}, \text{e.g., } \sigma_{\text{jump}}, \text{which has no analog equilibrium})\).

Fischer and Rehage showed how shear-thinning systems can be tuned by changing surfactant and salt composition, from a shear-thickening system to a material with a stress plateau \((\text{the rheological signature of banding})\) but without banding \[\{4.1\}\]. The shear and normal stresses apparently follow the Giesekus model, which is one of the simplest non-linear constitutive equations \((\text{comprising a Maxwell model with the simplest stress-de} \text{pendent relaxation time})\). A molecular understanding for this behavior is lacking.

With critical micelle concentrations of order a few parts per million, micelles entangle at astonishingly low dilutions. Amazingly, systems which shear-thin at concentrations of a few percent can undergo a shear-thickening transition at fractions of \(< 0.1\% \[\{27\}\, \{4\}\, \{46\}\]. This this shear-induced structure \((\text{SIS})\) is still undetermined; early suggestions for the mechanism included runaway micellar growth due to flow-alignment \[\{47\}\, \{48\]\, but the observed strain rate \((\text{order inverse milliseconds})\) is much slower than the necessary micellar reorientation time, of order \(\mu s\). It is probable that charge, which controls the dramatic increase in micellar length for concentrations near the overlap concentration \[\{49\}\], plays an important role. Like the shear-thinning systems, macroscopic “phase separation” occurs: Hu et al. \[\{44\}\] found a gel-like phase that forms upon increasing the applied stress, with the mean strain rate decreasing \((\text{see Figure 2})\) as more material turns into gel, and increasing again after complete conversion. The gel is observed to fracture in flow, and slightly shear-thins. Applying a strain rate above the critical strain rate induces immediate complete conversion. Attempts to visualize the SIS using cryo-TEM have given few clues to the microstructure \[\{33\}\]. Note that coexistence in the shear-thinning micelles occur under controlled strain rate conditions, while coexistence in this thickening system occurs for controlled stress; in both cases banding occurs in the radial direction, indicating banding at a common shear stress. These differences may be coincidences of the constitutive behaviors of the coexisting phases, or due to whether stress or strain rate ultimately determines the SIS.

Berret et al. \[\{51\}\] studied cetyltrimethylammonium tosylate (CTAT) micelles, and found shear-thickening phase separation under controlled strain rate conditions above a critical strain rate \(\gamma_c \sim \phi^{0.55}\) \((\text{an increase in } \gamma_c \text{ with } \phi \text{ was also found by Hu et al. \[\{46\}\]}\); this concentration dependence remains unexplained. The composite curve \(\sigma_{\text{jump}}(\gamma)\) has a positive slope, in contrast to the S curve of Ref. \[\{46\}\], possibly because the “thick” phase is not thick enough; alternatively, phase separation along the vorticity direction \((\text{at a common strain rate})\) would also be consistent with a positive slope \(d\sigma_{\text{p}}/d\gamma\) for the composite flow curve \[\{32\}\]. The SIS is shear-thinning, displays an oriented structure in neutron scattering, and does not have the extremely long recovery times found in Ref \[\{46\}\]. Qual-

![Figure 2: Qualitative constitutive curves for a shear-thickening system, such as the micellar system reported by Boltenhagen et al. \[\{45\}\, \{46\]\]. The thin curves denote single phase relations \((\text{micellar liquid or a gel-like material})\); the thick curve denotes the composite flow curve along which the material phase separates for controlled stress \(\sigma > \sigma_c\), and complete conversion to gel occurs for \(\sigma = \sigma_{\text{max}}\). Upon controlling the strain rate the system traverses between the two branches at \(\gamma_c\). Note that, if compositions of the coexisting phases were identical, the controlled-stress composite flow curve would be vertical.](image-url)
[32] McLeish T, Ed.: Proceedings of the NATO Advanced Study Institute on Theoretical Challenges in the Dynamics of Complex Fluids, Cambridge UK, volume 339 of E: Applied Sciences Kluwer, Dordrecht, 1997.

From a highly successful workshop in 1996, this summarizes the essentially still-current state of knowledge of the flow behavior of a wide variety of complex fluids.

[3] Milner ST, McLeish TCB: Reptation and contour-length fluctuations in melts of linear polymers. Phys. Rev. Lett., 1998, 81:725–728.

[4] McLeish TCB, Milner ST: Entangled dynamics and melt flow of branched polymers. In Advances in Polymer Science. Springer-Verlag, Berlin, 1999.

This recent review discusses several new advances in the molecular rheology of polymers with complex topology, including stars, H-polymer, and the “pom-pom” model (a toy branched polymer).

[5] Milner ST, McLeish TCB: Parameter-free theory for stress relaxation in star polymer melts. Macromolecules, 1997, 30:2159–2166.

[6] Marrucci G: Dynamics of entanglements: a nonlinear model consistent with the Cox-Merz rule. J. Non-Newton. Fl. Mech., 1996, 62:279–289.

[7] Ianniruberto G, Marrucci G: On compatibility of the Cox-Merz rule with the model of Doi and Edwards. J. Non-Newton. Fl. Mech., 1996, 65:241–246.

[8] Mead DW, Larson RG, Doi M: A molecular theory for fast flows of entangled polymers. Macromolecules, 1998, 31:7895–7914.

This work expands on the ideas of Ianniruberto and Marrucci, using convective constraint release to modify the Doi-Edwards picture at high strain rates.

[9] MacKintosh FC, Janmey PA: Actin gels. Current Opinion in Solid State & Materials Science, 1997, 2:350–357.

[10] Käs J, Strey H, Sackmann E: Direct imaging of reptation for semiflexible actin-filaments. Nature, 1994, 368:226–229.

Using fluorescent probes, individual macromolecules can be individually visualized, hence providing for direct confirmation of theoretical ideas such as Rouse modes and relaxation by reptation.

[11] Janmey PA, Hvidt S, Kas J, Lerche D, Maggs A, Sackmann E, Schliwa M, Stossel TP: The mechanical-properties of actin gels - elastic-modulus and filament motions. J. Biological Chemistry, 1994, 269:32503–32513.

[12] Gittes F, Schnurr B, Olmsted PD, MacKintosh FC, Schmidt CF: Microscopic viscoelasticity: shear moduli of soft materials determined from thermal fluctuations. Phys. Rev. Lett., 1997, 79:3286–3289.

This work introduces a new high-frequency, high-resolution optical technique for measuring the local moduli of soft materials, by recording the power spectrum of an entrapped bead fluctuating in a material.
[13] Mason TG, Ganesan K, van Zanten JH, Wirtz D, Kuo SC: Particle tracking microrheology of complex fluids. Phys. Rev. Lett., 1997, 79:3282–3285.

This is a complementary work to the work above, and also uses an optical technique to extract the elastic moduli of soft materials.

[14] Odijk T: On the statistics and dynamics of confined or entangled stiff polymers. Macromolecules, 1983, 16:1340–1344.

[15] Semenov AN: Dynamics of concentrated-solutions of rigid-chain polymers. 1: Brownian-motion of persistent macromolecules in isotropic solution. Journal of the Chemical Society-Faraday Transactions II, 1986, 82:317–329.

[16] MacKintosh FC, Kai J, Janmey PA: Elasticity of semiflexible biopolymer networks. Phys. Rev. Lett., 1995, 75:4425–4428.

[17] Maggs AC: Two plateau moduli for actin gels. Phys. Rev. E, 1997, 55:7396–7400.

[18] Bagley EB, Cabot IM, West DC: Discontinuity in the flow curve of polyethylene. J. Appl. Phys., 1958, 29:109–110.

[19] Vinogradov GV: Viscoelastic properties and flow of narrow distribution polybutadienes and polyisoprenes. J. Pol. Sci. A, 1972, 10:1061.

[20] Denn MM: Issues in viscoelastic fluid mechanics. Annu. Rev. Fluid Mech., 1990, 22:13–34.

[21] Cates ME: Reptation of living polymers—dynamics of entangled polymers in the presence of reversible chain-scission reactions. Macromolecules, 1987, 20:2289–2296.

[22] Turner MS, Cates ME: Linear viscoelasticity of wormlike micelles - a comparison of micellar reaction-kinetics. J. Phys. II (France), 1992, 2:503–519.

[23] Khutory A, Lequeux F, Kern F, Candau SJ: Linear and nonlinear viscoelasticity of semiflexible solutions of wormlike micelles at high-salt content. Lang., 1993, 9:1456–1464.

[24] Cates ME: Nonlinear viscoelasticity of wormlike micelles (and other reversibly breakable polymers). J. Phys. Chem., 1990, 94:371.

[25] Schmitt V, Marques CM, Lequeux F: Shear-induced phase-separation of complex fluids – the role of flow-concentration coupling. Phys. Rev., 1995, E52:4009–4015.
This is the first theoretical work describing the qualitative effects of concentration coupling on the effective rheological curves in shear banding flow; further, they distinguish when one may see phase coexistence with separation along the vorticity or flow gradient directions.

[37] Decruppe JP, Cressely R, Makhloufi R, Cappelaere E: Flow birefringence experiments showing a shear-banding structure in a CTAB solution. Coll. Polym. Sci., 1995, 273:346–351.

[38] Berret JF, Porte G, Decruppe JP: Inhomogeneous shear rows of wormlike micelles: a master dynamic phase diagram. Phys. Rev. E, 1997, 55:1668–1676.

[39] Cappelaere E, Berret JF, Decruppe JP, Cressely R, Lindner P: Rheology, birefringence, and small-angle neutron scattering in a charged micellar system: evidence of a shear-induced phase transition. Phys. Rev. E, 1997, 56:1869–1878.

[40] Berret JF, Roux DC, Porte G: Isotropic-to-nematic transition in wormlike micelles under shear. J. Phys. II (France), 1994, 4:1261–1279.

[41] Berret JF: Transient rheology of wormlike micelles. Lang., 1997, 13:2227–2234.

[42] Grand C, Arrault J, Cates ME: Slow transients and metastability in wormlike micelle rheology. J. Phys. II (France), 1997, 7:1071–1086. This is a careful study of transients in flow-induced phase separation. They explore metastability under both controlled strain rate and controlled stress conditions.

[43] Fischer P, Rehage H: Non-linear flow properties of viscoelastic surfactant solutions. Rheol. Acta., 1997, 36:13–27. This work demonstrates how CTAB/NaSal, at certain compositions, obeys the Giesekus constitutive model remarkably well.

[44] Wheeler EK, Fischer P, Fuller GG: Time-periodic flow induced structures and instabilities in a viscoelastic surfactant solution. J. Non-Newton. Fl. Mech., 1998, 75:193–208.

[45] Boltenhagen P, Hu YT, Matthys EF, Pine DJ: Observation of bulk phase separation and coexistence in a sheared micellar solution. Phys. Rev. Lett., 1997, 79:2359-2362.

[46] Hu YT, Boltenhagen P, Pine DJ: Shear thickening in low-concentration solutions of wormlike micelles. I. Direct visualization of transient behavior and phase transitions. J. Rheol., 1998, 42:1185–1208. This work presents a careful study of the appearance of a gel-like shear-induced structure in wormlike micelles, and contains visualizations of the bands.

[47] Cates ME, Turner MS: Flow-induced transitions in rod-like micelles. J. Phys. Cond. Matt., 1992, 4:3719–3741.

[48] Bruinsma R, Gelbart WM, Benshaul A: Flow-induced gelation of living (micellar) polymers. J. Chem. Phys., 1992, 96:7710–7727.

[49] MacKintosh FC, Safran SA, Pincus PA: Equilibrium size distribution of charged living polymers. J. Phys. Cond. Matt., 1990, 2:SA359–SA364.

[50] Keller SL, Boltenhagen P, Pine DJ, Zasadzinski JA: Direct observation of shear-induced structures in worm-like micellar solutions by freeze-fracture electron microscopy. Phys. Rev. Lett., 1998, 80:2725–2728.

[51] Berret JF, Gamezcorrales R, Oberdisse J, Walker LM, Lindner P: Flow-structure relationship of shear-thickening surfactant solutions. Europhys. Lett., 1998, 41:677–682. This work reports on a shear-thickening micellar system, and the authors extract the (increasing) dependence of the critical strain rate on concentration, as well as an activated temperature dependence.

[52] Hartmann V, Cressely R: Linear and non linear rheology of a wormlike micellar system in presence of sodium tosylate. Rheol. Acta., 1998, 37:115–121.

[53] Larson RG: Instabilities in viscoelastic flows. Rheol. Acta., 1992, 31:213–263.

[54] Malkus DS, Nohel JS, Plohr BJ: Dynamics of shear flow of a non-Newtonian fluid. J. Comp. Phys., 1990, 87:464–487.

[55] Español P, Yuan XF, Ball RC: Shear banding flow in the Johnson-Segalman fluid. J. Non-Newton. Fl. Mech., 1996, 65:93–109.

[56] Greco F, Ball RC: Shear-band formation in a Non-Newtonian fluid model with a constitutive instability. J. Non-Newton. Fl. Mech, 1997, 69:195.

[57] Spenley NA, Yuan XF, Cates ME: Nonmonotonic constitutive laws and the formation of shear-banded flows. J. Phys. II (France), 1996, 6:551–571.

[58] Porte G, Berret JF, Harden JL: Inhomogeneous flows of complex fluids: Mechanical instability versus non-equilibrium phase transition. J. Phys. II (France), 1997, 7:459–472.