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 γ above an inverse reptation time τ_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 τ_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 at 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 $L_p < L_e$, the distance between entanglements or confinement constraints (or deflection length [14]), one expects the behavior of flexible 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 [CPCl/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.* CPCl) 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 (the geometric mean of the reptation and breaking times) [26], in quantitative agreement with experiment [•27].

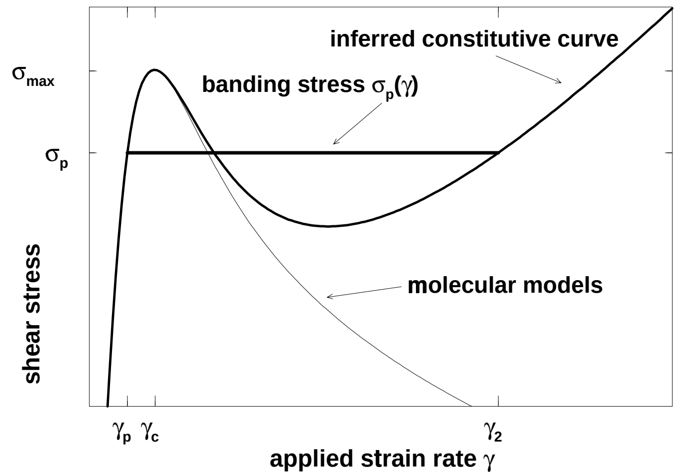

Figure 1: Model constitutive relation $\sigma(\gamma)$ for a shear-thinning complex fluid with a bulk instability (after Ref. [29]). The thick curve shows the kind of curve envisioned for wormlike micellar solutions: this one is from the Johnson-Segalmann model [54]. Portions of the curve with negative 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 γ_c. Convected constraint release [•8] 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 γ_2 and a portion at the low shear rate $\gamma_1 = \gamma_p$. A dependence of σ_p on γ (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 [••36, ••32].

The non-linear rheology of micellar systems was first studied by Rehage and Hoffman [•27], who discovered dramatic shear thinning (analogous to the DE instability) and shear-thickening, depending on the salt/surfactant/water composition. The shear-thinning systems were the first to be systematically studied (see Figure 1). Above a critical strain rate γ_p an apparent phase separation into macroscopic coexisting regions occurs, at a reproducible and history-independent stress σ_p, in which the high strain rate material is well aligned (typically birefringent) and the low strain rate material remains relatively disordered. The underlying flow curve has the stress maximum σ_{max} (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 $\sigma > \sigma_p$ [29].] This occurs in semi-dilute systems, of order a few percent surfactant [28], or in more concentrated systems (of order 30%) with a nearby equilibrium nematic transition [30, 31]. In the former case the dynamic instability is believed to be polymeric 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. [33] 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, ••32], indeed seen in concentrated solutions which often have an underlying nematic transition [37, 38, 39, •34].

Groups have begun investigating metastability. Berret *et al.* [40, 41] 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 $\sigma \sim \exp - \{t/\tau(\gamma)\}^{\alpha}$, $(\alpha = 2)$, which they interpreted as one-dimensional nucleation and growth. Grand *et al.* [•42] studied transients in more dilute ($\sim 1\%$) 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 γ_p at the onset of banding. They also performed controlled stress experiments, and discovered a stress $\sigma_{jump} > \sigma_p$, 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 (given, *e.g.*, σ_{jump}, which has no equilibrium analog).

Fischer and Rehage showed how shear-thinning systems can be tuned by changing surfactant and salt composition, from a shear banding material to a material with a stress plateau (the rheological signature of banding) but *without* banding [•43]. The shear and normal stresses apparently follow the *Giesekus model*, which is one of the simplest non-linear constitutive equations (comprising a Maxwell model with the simplest stress-dependent 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, 44, ••46]. This this shear-induced structure (SIS) is still undetermined; early suggestions for the mechanism included runaway micellar growth due to flow-alignment [47, 48], but the observed strain rate (of order inverse milliseconds) is much slower than the necessary micellar reorientation time, of order μs. 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.* [••46] found a gel-like phase that forms upon increasing the applied stress, with the mean strain rate decreasing (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 [50]. 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.

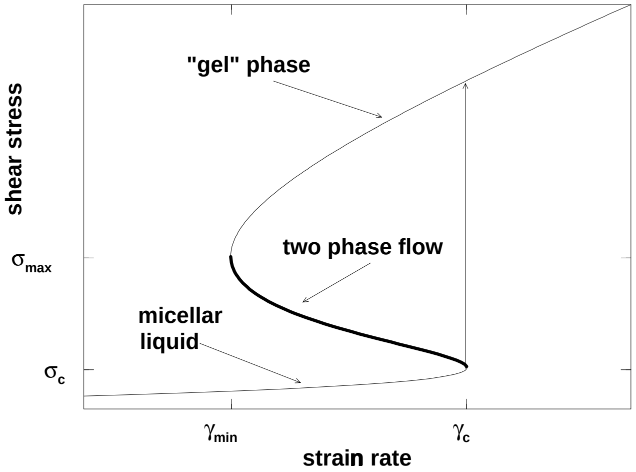

Figure 2: Qualitative constitutive curves for a shear-thickening system, such as the micellar system reported by Boltenhagen *et al.* [45, ••46]. The thin curves denote single phase relations (micellar liquid or a gel-like material); the thick curve denotes the composite flow curve along which the material phase separates for controlled stress $\sigma > \sigma_c$, and complete conversion to gel occurs for $\sigma = \sigma_{max}$. Upon controlling the strain rate the system traverses between the two branches at γ_c. Note that, if compositions of the coexisting phases were identical, the controlled-stress composite flow curve would be vertical.

Berret *et al.* [•51] studied cethyltrimethylammonium tosylate (CTAT) micelles, and found shear-thickening phase separation under controlled *strain rate* conditions above a critical strain rate $\gamma_c \sim \phi^{0.55}$ (an increase in γ_c with ϕ was also found by Hu *et al.* [••46]); this concentation dependence remains unexplained. The composite curve $\sigma_p(\gamma)$ 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 (at a common strain rate) would also be consistent with a positive slope $d\sigma_p/d\gamma$ 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]. Qualitatively similar data were reported for a CTAB-NaTOS solution by Harmann and Cressely [52]. We finish our (incomplete) zoo of micellar thickening transitions by mentioning yet another study on CPCl/NaSal: revisiting early experiments by Rehage, Wheeler *et al.* [44] found spatio-temporal instabilities consisting of dark and light oscillating vertical bands (in cylindrical Couette flow); these accompany formation and destruction of new microstructure (evident from turbidity), and are suggestive of a Taylor-Couette elastic instability [53].

Athough wormlike micelles can have much simpler rheology than their polymer cousins due to the frequent presence of a single relaxation time in the fast breaking limit, this simplicity is delicate, and strong flows can dramatically affect the micelle microstructure. We are far from a general molecular theory for these transitions, and do not even *know* the nature of the microstate in most cases. Continuum constitutive models may provide some insight, although when these models succeed we usually do not know why (*e.g.* The Giesekus model [•43]). A popular constitutive model is the local Johnson-Segalman model [54], which is relatively simple and displays the non-monotonic flow curve characteristic of shear-thinning micelles. Numerical calculations [55, 56] resemble some startup experiments [41], and authors have attempted to determine plateau stress σ_p for the onset of banding in this model [54, 56]. It has become apparent that this, or any local, model does not give a unique selected banding stress [57], and an additional assumption is necessary [58, ••32]. There is growing consensus that non-local (*i.e.* gradient terms) contributions to constitutive equations supply an unambiguous determination of the plateau stress [••32].

4 Outlook

Despite progress in understanding of flexible and semiflexible polymer dynamics, there is no shortage of problems for the immediate future. We lack a credible complete molecular understanding for *any* of these micellar flow-induced transtitions: such a model must presumably include charge and concentration, as well as polymeric effects, to account for the (still unknown, in most cases!) structural changes under flow. By comparing and contrasting living and non-living polymers we may be able to extract important physics. Besides these systems, many other complex fluid systems undergo a variety of flow-induced phase transitions, and it seems reasonable to hope that this variety of transitions may be put on a common ground, akin to the thermodynamics of equilibrium phase transitions.

I am indebted to J-F Berret, ME Cates, SL Keller, CYD Lu, FC MacKintosh, TCB McLeish, DJ Pine, and G Porte for much discussion and advice.

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