

## Simulating Polymers in Sheared Drops

O. Berk Usta<sup>1</sup>, Julia M. Yeomans<sup>2</sup> and Anna C. Balazs<sup>1</sup>

<sup>1</sup> Chemical and Petroleum Engineering Department, University of Pittsburgh, Pittsburgh, PA, 15261, USA

<sup>2</sup> Rudolf Peierls Centre for Theoretical Physics, University of Oxford, 1 Keble Rd., Oxford OX1 3NP, UK

### Abstract

Using computational modeling, we investigate the shear response of a droplet that encases a dilute concentration of polymers and nanoparticles. We show that the viscoelastic effects of the encapsulated polymers reduce the shear-induced deformation of the droplet at intermediate capillary numbers, but can induce the breakup of the droplet at high capillary numbers.

Microscopic droplets that encapsulate particles or polymers are critical components in a tremendously diverse range of technological applications, from inkjet printing to drug discovery.<sup>1</sup> Either in their fabrication or end use, the filled droplets are suspended in a flowing immiscible phase, which acts to maintain the discrete nature of the drops and propel these micro-carriers to their target sites. Determining the factors that control the properties of this multi-phase mixture is a daunting task because the following processes occur simultaneously within the system: phase-separation between the host and droplet fluids, deformation of the droplet due to the imposed flow, wetting interactions between the encapsulated species and the droplet, viscoelastic effects arising from the encased polymers, and hydrodynamic interactions among all the components.<sup>2,3</sup> On the one hand, these processes could collectively contribute to splitting the droplet into smaller domains or on the other hand, could inhibit the breakup of the droplet as it is sheared by the carrying fluid. Establishing which of these scenarios will occur is vitally important for optimizing the utility and performance of the filled droplets.

Therefore we introduce a hybrid computational approach to determine the effects of an imposed simple shear flow on an A droplet that encapsulates a dilute concentration of polymers or nanoparticles; this filled droplet is immersed in an immiscible B phase. In the simulations, we integrate a mesoscale model for the fluid dynamics with a particle-based description of the encapsulated species, and thereby capture the hydrodynamic interactions among all the constituents. Through this approach, we can probe the effects of varying the particle concentration and the length of the chains. We show that although the expectation that viscoelastic effects reduce the deformation of a drop holds at intermediate capillary numbers, the situation is more complex at high capillary numbers where the polymers can actually contribute to premature breakup of the drop. We find that the flow field inside the droplet and the droplet shape play a significant role in determining the effect of the suspended phases, which in turn affect the stability of the drop.

The ingredients which make up our model are:

- (i) an immiscible binary fluid, with two phases A,B, described using a Landau free energy functional, and obeying the Navier-Stokes equations of motion.
- (ii) particles, or polymer chains modeled as particles connected by springs.
- (iii) a wetting interaction such that the particles prefer to lie in the A phase.
- (iv) hydrodynamic coupling between particles and fluid.

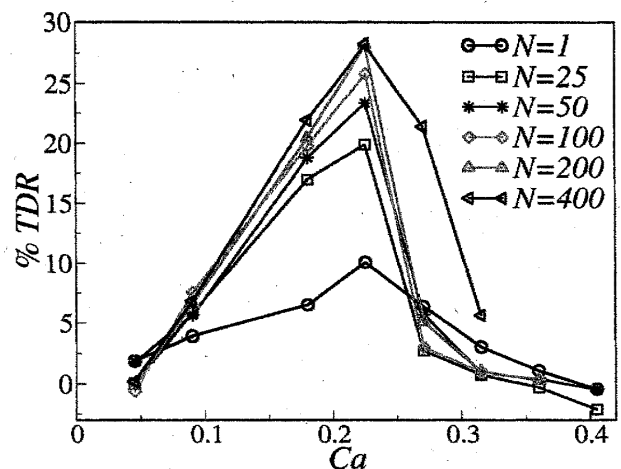
The equations of motion of the fluid are solved using a lattice Boltzmann algorithm. The particles obey Newton's equation of motion which are integrated using a first order implicit scheme. Further details can be found in refs. <sup>4,5,6</sup>.

An initially spherical A drop is suspended in the B phase and the fluid is subjected to shear. We ramp up the shear rates sufficiently slowly that transient breakup due to inertia is avoided. The response of the A droplet to the imposed shear is dictated by the capillary number,  $Ca = \eta\dot{\gamma}R/\sigma$ , which describes the effects of the viscous stresses relative to the interfacial stresses in the system. The capillary number in our simulations spans the range  $0.045 \leq Ca \leq 0.405$ , and correspondingly, the Reynolds number,  $Re = \rho\dot{\gamma}R^2/\eta$ , extends over the range  $0.94 \leq Re \leq 8.44$ . Under modest deformation, we characterize the distortion of the drop due to the imposed flow via the Taylor deformation parameter,  $TD = (L - S)/(L + S)$ , where  $L$  and  $S$  are the respective "long" and "short" axes of an ellipse that approximates the shape of the sheared drop.

We first determine the deformation of the "pure" A droplet (without encased species) at several different shear rates (i.e.,  $Ca$ ). We then repeat these simulations for the filled droplets. To assess the effect of the encapsulated polymers and nanoparticles, we define the relative reduction in Taylor deformation,  $\%TDR = (TD_{pure} - TD_s)/TD_{pure} \times 100$  where  $TD_{pure}$  refers to the deformation of the pure A droplet and  $TD_s$  refers to the deformation of a drop with suspended species. Due to fluctuations in the system, we present the time averaged values in our figure.

Figure 1 shows the deformation of various filled drops as a function of  $Ca$ . For ease of comparison we keep the number of hydrodynamic centers constant at  $n = 400$  (area fraction  $\sim 10\%$ ) and compare the relative effects of chains with lengths  $N = 25, 50, 100, 200$  and  $400$  monomers, and nanoparticles ( $N = 1$ ). (A chain of 400 monomers has a radius of

Figure 1 a) Reduction in Taylor deformation (TDR) for a drop containing 400 point particles joined to form chains with differing molecular weights.



gyration slightly larger than the radius of the undeformed drop.) We analyze our results in terms of three regimes: “low” ( $Ca < 0.1$ ), “intermediate” ( $Ca \sim 0.15-0.25$ ) and “high” capillary numbers ( $Ca > 0.35$ ).

At low  $Ca$ , the deformation of the pure drop is small and neither the polymers nor the nanoparticles have a significant impact. This is because in this regime, the flow inside the droplet is predominantly rotational despite the imposed shear flow and, hence, the viscous and elastic stresses are relatively weak.

By increasing  $\dot{\gamma}$ , we attain the intermediate  $Ca$  regime; the flow inside the droplet now exhibits a significant extensional component, which is sufficiently large to stretch the polymers and thus, induce extra elastic stresses in the system. The flow-induced chain stretching is resisted by entropic restoring forces, leading to a cyclic stretching and coiling or tumbling of the polymers in the flow. The stretch-coil (or stretch-tumble) transition is more pronounced for longer chains. This dynamic behavior has been experimentally observed in single polymer chains in steady shear flow.<sup>7</sup> In confined geometries, the repeated retraction of a stretched chain is particularly pronounced<sup>8</sup> because the chains are typically localized in the center of the domain (or droplet), where the velocity is the smallest and consequently, there is insufficient force to maintain the chains in the stretched state; the small fluctuations in the chain’s center of mass position dictates whether the chain is temporarily extended by the neighboring flow or collapses near the center of the droplet. Because the chains and fluid are coupled through the wetting interactions and frictional forces, the droplet also displays this “yo-yo like” behavior, as shown in Fig. 2. The overall (time-averaged) effect of these polymer-induced structural changes is to significantly reduce the flow-induced deformation of the droplet. In particular, the long polymers can reduce the deformation by as much as  $\sim 28\%$ , while even the shortest chains considered here produce a reduction of  $\sim 18\%$ . By comparison the nanoparticles reduce the deformation by only approximately 10% at  $Ca = 0.225$ ; this clearly indicates the significance of elastic contributions when polymers are present in the droplet.

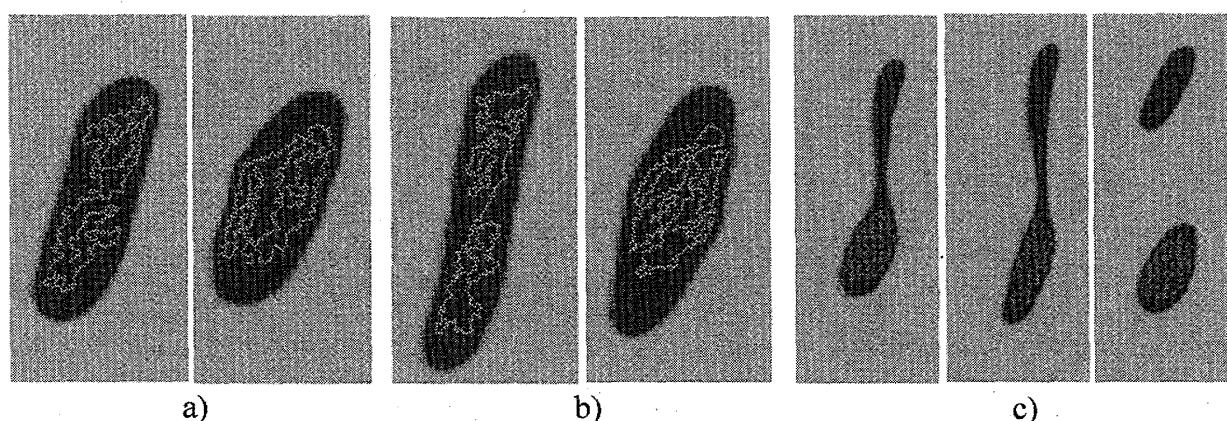


Figure 2 Snapshots of a drop encapsulating a long polymer chain ( $N=400$ ) illustrating the “yo-yo” like viscoelastic effects. (a)  $Ca=0.225$  (b)  $Ca=0.27$  (c) Break up at  $Ca=0.36$ . Note that the bead radii are not drawn to scale in order to illustrate their locations.

The transition from intermediate to high  $Ca$  reveals a surprising and dramatic effect: the deformation reduction ( $\%TDR$ ) produced by the chains decreases abruptly from a maximum to almost nil. This drastic change stems again from a qualitative change in the flow

profiles and drop shape. The drop goes from an elliptic shape to a dumbbell, with a long neck that is roughly aligned with the flow axis. The flow in the neck is a simple shear flow, whereas the lobes of the dumbbell encompass strong, locally rotational flows. Due to this rotational flow, along with the higher velocity in the lobes, the polymers become trapped in these domains and collapse; consequently, they can no longer exert either viscous or elastic stresses. (Note that there exists a finite probability of escaping these lobes that decreases with increasing chain length.)

At  $Ca \geq 0.35$  the drop transitions from a two lobed to a three lobed structure and neither of the lobes is sufficiently large to accommodate the longest chains. Since these long polymers favor the A phase, they effectively withdraw fluid from the already thin necks; this behavior is driven not only by the wetting interactions, but also by the high cost in free energy of having an extended, narrow A region in the B bulk. Consequently, for  $N = 400$  the neck “snaps off” at  $Ca = 0.36$  and the droplet ruptures into two smaller droplets, with one of these droplets enclosing the polymer chain. In this manner, the long polymers induce a droplet breakup, which is not observed for either the pure or nanoparticle filled drop at these  $Ca$  values. We note that shorter chains can also induce breakup at  $Ca = 0.405$  with a probability that increases with increasing chain length.

To summarize, a striking feature that emerges from these simulations is the complex interplay that exists between the flow field inside the droplet and the dynamics of the encapsulated chains at intermediate and high  $Ca$ . In particular, the flow field distorts the chains, which in turn perturb the shape of the droplet. At intermediate  $Ca$ , the elongational component of the flow within the droplet is sufficiently high to stretch the polymers, which then undergo a yo-yo like motion within the droplet. Averaged over time, these chain dynamics significantly affect the imposed shear and thus, diminish the overall deformation of the droplet. At higher  $Ca$ , the deformation of the droplet dominates, with the relatively strong rotational flow trapping the polymer in the outer lobes of a dumbbell. Confined in this region, long, A-like chains induce a premature breakup of the drop. Overall, these findings indicate guidelines for tailoring both the processing conditions and the components of filled droplets to achieve the desired performance in various technological applications.

## References

1. S.-Y. Teh, R. Lin, L.-H. Hung and A. P. Lee, *Lab Chip*, 2008, 8, 198-220; K. A. Smith, M. Ottino and M. Olvera de la Cruz, *Phys. Rev. Lett.*, 2004, 93, 204501.
2. H. Li and U. Sundararaja, *Phys. Fluids*, 2008, 20, 053101.
3. G.H. McKinley in *Rheology Reviews*, 2005, 1-48, ed. D.M. Binding and K. Walters, British Society of Rheology.
4. R. Verberg, J. Yeomans and A. C. Balazs, *J. Chem. Phys.*, 2005, 123, 224706.
5. O. B. Usta, A. J. C. Ladd and J. E. Butler, *J. Chem. Phys.*, 2005, 122, 094902.
6. P. Ahlrichs and B. Dünweg, *J. Chem. Phys.*, 1999, 111, 8225-8239.
7. D. E. Smith, H. P. Babcock and S. Chu, *Science*, 1999, 283, 1724-1727.
8. N. Watari, M. Doi, R. G. Larson, *Phys. Rev. E*, 2008, 78, 011801.