

# The origin of contact line forces during the retraction of dilute polymer solution drops

M.I. Smith\* and J.S. Sharp

*School of Physics and Astronomy and Nottingham Nanotechnology and Nanoscience Centre,  
University of Nottingham, University Park, Nottingham, NG7 2RD, UK*

E-mail: [mike.i.smith@nottingham.ac.uk](mailto:mike.i.smith@nottingham.ac.uk)

*This document is the unedited Authors version of a Submitted Work that was subsequently accepted for publication in Langmuir, copyright 1999 American Chemical Society after peer review. To access the final edited and published work see <http://pubs.acs.org/doi/abs/10.1021/la5005159>*

## Abstract

The forced dewetting of water and dilute polyethylene oxide solution (PEO) drops is investigated for a syringe driven flow. Comparisons are made with the free dewetting observed during drop impact. We provide strong evidence that during droplet retraction, polymer deposited on the substrate results in a velocity dependent force at the contact line. These findings are in stark contrast to previous studies which attributed dissipation to bulk visco-elastic effects or normal stress effects at the contact line.

## Introduction

Control of the wetting of liquid drops is an important consideration in a number of technological applications including contact dispensing,<sup>1</sup> inkjet printing,<sup>2</sup> spray cooling<sup>3</sup> and application of

---

\*To whom correspondence should be addressed

agrochemicals.<sup>3,4</sup> Deposition of drops during these processes involves a rapidly moving contact line, often initiated by a drop impacting a surface. A number of strategies have been investigated to provide the necessary control, including altering the surface wettability,<sup>5</sup> electrowetting deposition,<sup>6</sup> or liquid bridge break up.<sup>1</sup> Whilst the drop impact dynamics of simple fluids have been extensively studied<sup>5</sup> there is an increasing research effort to understand the influence of additives such as nanoparticles, surfactants and polymers.<sup>4,7,8</sup> These additives can influence the dynamic wetting and de-wetting of droplets via a variety of mechanisms such as pinning of the contact line,<sup>7</sup> dynamic surface tension effects<sup>8</sup> or simply altering the physical properties (such as the shear viscosity) of the droplet.

One dramatic example of the effects of additives occurs when  $\sim 100 \mu\text{gml}^{-1}$  of a high Mw polymer, such as Poly-(ethylene oxide) (PEO), is added to water. If a water drop impacts a hydrophobic surface, it expands to form a flat disc ( $V_{\text{spread}} \sim 1000 \text{mms}^{-1}$ ) before contracting under the action of surface tension ( $V_{\text{retraction}} \sim 200 \text{mms}^{-1}$ ). If insufficient viscous dissipation has occurred then the drop will rebound from the surface. Drops containing long polymer chains also spread rapidly, but then retract an order of magnitude more slowly ( $V_{\text{retraction}} \sim 20 \text{mms}^{-1}$ ). A PEO solution drop is therefore much less likely to rebound from a surface.

Initially, the energy dissipation mechanism in impacting dilute polymer solution drops was thought to be caused by a transient increase in the extensional viscosity. It was believed that velocity gradients, generated in the fluid, stretched the polymer chains leading to increased energy dissipation and slow retraction.<sup>4</sup> However, it has recently been shown that the slowing of the retracting fluid is dominated by the properties of the contact line rather than bulk flow.<sup>3,9-11</sup>

Other studies have considered the role of the substrate during the retraction of drops of dilute polymer solutions. Drops impacting small targets and drops impacting hot surfaces (such that a Leidenfrost layer developed between the drop and surface) were shown to rebound and not exhibit the reduced retraction velocities observed for the same drops on solid surfaces.<sup>12,13</sup> However, the significance of these results must be carefully interpreted since by removing the surface, the flows inside the drop may also have been altered. Bartolo et al<sup>3</sup> have suggested that the anti-rebound

effect relies upon the no slip boundary condition provided by the substrate in order to generate a shear flow in the vicinity of the contact line. They argue that the resultant velocity gradient generates normal stresses in the polymer solution which leads to enhanced energy dissipation. These authors obtained indirect evidence which suggested that polymer deposition was *not* the origin of the phenomenon, by observing the impact dynamics of water drops on substrates which had been previously dipped into dilute polymer solutions. The role of the surface was therefore believed to be the generation of a shear flow at the contact line of the drop and not a direct interaction with adsorbed polymer chains. However, more recently the biopolymer  $\lambda$ -DNA was observed to weakly suppress drop rebound. These polymer chains were observed to stretch at the retreating contact line and were deposited on the substrate in a stretched conformation.<sup>9</sup> This suggests that an interaction between substrate and polymer chains does exist and that it may play an important role in the anti-rebound effect. The confusion over the role of the surface generated by these contradictory results<sup>3,9,10</sup> requires additional consideration, and is the focus of this paper. However, the wider issues of dynamic wetting in additive containing droplets, addressed by this study are likely to be of broader interest.

## Materials and methods

To investigate the role of the substrate in the anti-rebound phenomenon we simulated drop impact using a syringe pump. A glass capillary was placed close to a hydrophobic surface and 0.5ml of fluid was dispensed. Upon reaching the maximum dispensed volume, the direction of pumping was reversed, sucking the drop back into the capillary. This results in a maximum retreating contact line velocity which is comparable to that observed during drop impact experiments of dilute polymer solutions ( $V_{max} \sim 16 \text{ mms}^{-1}$ ).

A series of measurements were performed, in which the drops were spread on the surface using a flow rate of  $485 \mu\text{ls}^{-1}$  and then retracted at constant flow rates of 485, 345, 165, 55, 21 and  $6 \mu\text{ls}^{-1}$ . The radial symmetry of the drops means that a constant volume flow rate resulted in

a contact line velocity that varies with radius. Movies of the expansion and retraction of each drop were captured using a Dalsa Genie HC640 equipped with a 10x Macro lens at frame rates varying from 5-200fps. The macroscopic contact angles and diameter of the drops in each frame were then measured using image processing software written in Matlab (see supplementary information 1).

The experiments were performed with solutions of pure water and  $200\mu\text{gml}^{-1}$  PEO ( $M_w \sim 4 \times 10^6$ , Sigma) were dissolved in deionised water. The surface tensions of water drops and the PEO solution drops were measured using the pendant drop technique<sup>14</sup> and found to be  $72 \pm 2 \text{ mNm}^{-1}$  and  $64 \pm 3 \text{ mNm}^{-1}$  respectively which are consistent with literature values.<sup>3,12,13</sup> Drop retraction experiments were performed on glass slides spin coated with a 120nm thick polystyrene (PS) film. The rms roughness of a spin cast PS film was measured to be  $\sim 1 \text{ nm} \pm 0.4$  over a  $20\mu\text{m}$  square area using atomic force microscopy.

Drop impact experiments were also performed with the same solutions and surfaces. Droplets were formed at the end of a blunt 21G hypodermic needle and dropped onto a PS surface from a height of 12cm. The dynamics were filmed with an Optronis CL 600X2 high speed camera at 500fps.

## Results and Discussion

Drop impact studies and syringe driven flows have important differences but they both exhibit the same key features of interest to this study; namely a retreating contact line moving across a hydrophobic surface at comparable velocities (for PEO solution drops). The use of a syringe driven drop retraction also provides two big advantages. Firstly, the motion of the retracting contact line can be carefully controlled. This enables slow retraction velocities to be investigated, which are experimentally inaccessible in drop impact experiments. Secondly, oscillations of the bulk drop shape (which can obscure some of the details of the contact line motion in drop impact<sup>9</sup>), are not present in a syringe driven drop retraction. In this paper we elucidate some of the key aspects of the dewetting of dilute polymer drops using syringe driven flows before confirming the applicability

of these results to droplet impact phenomena.

Figure 1A shows example plots for a water drop ( $\square$ ) in which the fluid is retracted at the slowest flow rate of  $6\mu\text{ls}^{-1}$ . On the timescale of these experiments, evaporation is negligible ( $0.004\mu\text{Ls}^{-1}$ ) and therefore not expected to play a significant role. A similar plot is shown for the maximum flow rate of  $485\mu\text{ls}^{-1}$  in figure 1B. PS is hydrophobic with equilibrium contact angles for water and  $200\mu\text{gml}^{-1}$  PEO of  $\theta_{eq} \sim 87^\circ \pm 3$  and  $\sim 76^\circ \pm 3$  respectively. During the spreading of water drops we observed an approximately constant advancing contact angle ( $\theta_A \sim 97^\circ \pm 3$ ). Upon reaching the maximum radius, the pump flow direction is reversed (Left hand dashed line fig 1A). Initially, the contact line remains static with a steadily decreasing contact angle. At a receding contact angle ( $\theta_R \sim 76^\circ \pm 2$ ), the contact line begins to move (Right hand dashed line in fig 1A). In the case of water this contact angle  $\theta_R$  is found to vary by approximately  $6^\circ$  over the velocity range studied here (fig 2).<sup>15,16</sup> However, the uncertainties associated with determination of the contact angles are comparable to the observed changes (see experimental scatter in figures 1 and 2).

The macroscopic advancing and receding contact angles of PEO solution drops ( $\triangle$ ) were found to be lower than for water drops. This is due to the different balance of interfacial energies associated with the drops. At the lowest flow rate ( $6\mu\text{ls}^{-1}$ ) we observe strong qualitative similarities between the behaviour of water and PEO solutions (fig 1A). Upon reaching the maximum radius, the drop contact angle slowly decreases following a change in the flow direction. At a critical contact angle, the contact line begins to move and the contact angle is only weakly dependent upon velocity (see movie S1).

At the maximum flow rate ( $485\mu\text{ls}^{-1}$ ) the onset of retraction in the PEO solution drop occurs at approximately the same contact angle of  $\sim 63^\circ$  observed for slower retraction velocities (fig 1B). However, from this point onwards the behaviour of drops containing PEO deviates significantly from that of the corresponding water drop. Once the drop edge has begun to move, the contact angle rapidly decreases as the velocity of the contact line increases (see movie S2).

For a simple water drop the retracting contact line begins to move once  $\theta(t) \sim \theta_R$ . Any initial resistance to contact line motions arises due to surface roughness and heterogeneity.<sup>17,18</sup> Further

decreases in contact angle  $\theta(t) < \theta_R$  originate from additional forces ( $f$ ) acting per unit length along the contact line, where<sup>19</sup>

$$f = \gamma_{LV}(\cos\theta(t) - \cos\theta_R) \quad (1)$$

Although strictly only valid at equilibrium, the above equation is approximately correct since the retraction rate is slow enough for inertial effects to be neglected. Figure 2 shows a plot of the contact angle against contact line velocity during the retraction phase for all of the data collected. The contact angle for pure water drops (squares) is found to be largely independent of velocity. However, for drops of PEO solution (triangles) the contact angle decreases with increasing contact line velocity, indicating the presence of a velocity dependent force which resists the motion of the contact line. Equation 1 provides an estimate that the additional contact line force per unit length for PEO solution drops, retracting at  $16 \text{ mms}^{-1}$  is  $\sim 33 \text{ mNm}^{-1}$  (see supplementary information).

To determine whether the altered contact line dynamics in PEO solution drops are caused by the interaction of the fluid and adsorbed polymer chains we performed a series of experiments that were designed to isolate the effects of surface adsorbed polymer molecules. In the first instance we performed tapping mode atomic force microscopy (AFM) measurements on polystyrene (PS) films following the spreading and retraction of PEO drops to determine whether PEO is actually deposited at a surface by a retreating contact line (See supplementary information 4 for details). Figure 3 shows  $10 \times 10 \mu\text{m}$  AFM phase images for samples prepared using a retraction rate of 6 and  $485 \mu\text{ls}^{-1}$ . At the slow retraction rate, no structure is observed. However, at the fast retraction rate, long closely spaced chain-like structures were observed which were aligned ( $\pm 20^\circ$ ) with the radial direction corresponding to the drop centre. These structures are reminiscent of those observed previously for DNA chains.<sup>9</sup>

To determine the role of the deposited PEO we then performed a two stage experiment. Stage one: drops of  $200 \mu\text{gml}^{-1}$  PEO were spread at  $485 \mu\text{ls}^{-1}$  and then retracted at flow rates of 485, 278, 56,  $6 \mu\text{ls}^{-1}$  on glass slides coated with PS films. The capillary was positioned above a cross marked on the reverse side of the slide to enable the location of drop deposition to be easily de-

terminated. Following this the substrates were rinsed thoroughly with deionised water and dried with  $N_{2(g)}$ . Stage 2: a capillary of pure water was then positioned above the mark on the same glass slide and an experiment was performed in which both spreading and retraction occurred at the maximum flow rate of  $485\mu\text{ls}^{-1}$ .

Figure 3 shows the retraction dynamics for water drops in the two stage experiment. When the substrates were prepared with a PEO solution drop that had been retracted slowly, the behaviour of the water drops in stage 2 was very similar to that of a water drop spreading on a clean PS surface. However, when the substrate was preprepared with a PEO solution drop retracted at high speed, the subsequent retraction dynamics of the water drop resembled those of a drop containing PEO. This may explain why dipping substrates in PEO solutions, performed in a previous study,<sup>3</sup> did not alter the subsequent water droplet dynamics. Regardless, this simple observation provides extremely strong evidence that the deposition of polymer chains on a surface has a significant effect upon contact line dynamics in retracting liquid droplets. This is the case even when there is no polymer dissolved in the bulk of the drops.

From these combined experiments it is clear that the interaction between the droplet and the polymer deposited on the surface is the dominant energy dissipation mechanism during the retraction of PEO solution drops. Figure 4a shows a comparison of the dynamics observed for three different droplet experiments all retracted at a flow rate of  $485\mu\text{ls}^{-1}$ . A comparison of the plots for the PEO solution drop on fresh PS surfaces and that of a water drop in the two stage experiment shows that the retraction dynamics are indistinguishable in these two cases within the limits of experimental uncertainty. Figure 2 also shows the equivalent contact angle against velocity data to be very similar. This provides strong evidence that polymer adsorbed to the surface can modify the contact line dynamics of a water droplet in the same way as is observed in droplets containing PEO.

One possible objection to the above is that the polymer might redissolve in the fluid during spreading influencing the rheology of the fluid. Two lines of evidence rule out this possibility. Firstly, estimates based upon the AFM images show that if all the polymer on the surface and in

contact with the base of the water drops were to redissolve in the fluid, the hypothetical polymer concentration would not exceed  $\sim 0.25 \mu\text{gml}^{-1}$  (See supplementary info 6.). This excludes any potential fluid rheology effects as a possible mechanism because such low concentrations would be expected to have little or no effect on droplet dynamics.<sup>9</sup> Furthermore, in performing these experiments the surfaces were rinsed with water following the PEO drop retraction and prior to the water drop measurement, thus ensuring that any polymer that could potentially redissolve had been removed from the surface.

Having established the origin of the dissipative forces at the contact line of retreating PEO drops we now show that such results are also applicable to droplet impact phenomena. Firstly, we confirmed that polymer is deposited at the surface following PEO drop impact using AFM (Figure S1). Secondly, a series of experiments, analogous to those conducted with the syringe pump, were conducted. Three types of drop impact experiments were performed. Upon impact on clean PS surfaces, water drops ( $\square$ ) were observed to spread and retract rapidly ( $\sim 10\text{ms}$ ) resulting in a partial rebound from the surface in which approximately half of the droplet was ejected. In contrast, the impact of a  $200 \mu\text{gml}^{-1}$  PEO drop ( $\triangle$ ) resulted in a retraction that was  $\sim 2$  orders of magnitude slower (see figure 4b). In the final drop impact experiment, a single drop of PEO was allowed to impinge and retract on a clean PS surface. The surface was then rinsed thoroughly with deionised water and dried. A droplet of pure water was then deposited on exactly the same spot that the PEO drop had been previously deposited ( $\circ$ ). Supplementary movie S3 shows an example of each type of experiment (the spreading and retraction dynamics are also plotted in figure 4b). It is clear that the dynamics of the water droplet, dropped onto a surface pretreated with a PEO drop shows very similar dynamics to that of a PEO drop on a clean PS surface i.e. the rebound effect observed for pure water on clean PS is suppressed by depositing a PEO drop first. This verifies that the forced dewetting experiments can be used to probe the physics of drop retraction of polymer loaded drops under conditions that are comparable to those observed in drop impact studies.



## Conclusions

Forced dewetting of droplets using a syringe pump was used to probe the origin of contact line forces during the retraction of PEO drops. It was shown that the force at the contact line increases with increasing retraction velocity. This force was shown to be correlated with the deposition of polymer chains at the surface. A novel two stage experiment in which pure water droplets were retracted on the same spot that a PEO droplet had previously been retracted was then performed. These water droplets displayed quantitatively similar dynamics to the PEO drops, suggesting that the dissipation arising at the contact line can be explained in terms of polymer deposited at an interface by the retreating contact line rather than in terms of the fluid rheology. Finally, using drop impact experiments we were able to confirm that our results are more generally applicable and provide a key insight into the mechanism responsible for the well known anti-rebound effect observed in drops of dilute polymer solution.

Supporting Information Available: 3 movies: Spreading and retraction of  $200\mu\text{gml}^{-1}$  PEO droplets at low and high speed. A side by side comparison of droplet impact of a water drop,  $200\mu\text{gml}^{-1}$  PEO drop and two stage experiment (details described in main text) 1 pdf: contains additional details of methods, supporting calculations and an AFM image of polymer left behind on the surface after a PEO drop impact experiment. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## Acknowledgement

We thank Dr V. Bertola for helpful discussions. MIS acknowledges a Royal Society University Research Fellowship. Funding is acknowledged from EPSRC grants EP/L003651/1 and EP/H004939/1.

## References

- (1) Qian, B.; Loureiro, M.; Gagnon, D.A.; Tripathi, A.; Breuer, K.S. Micron-Scale Droplet Deposition on a Hydrophobic Surface Using a Retreating Syringe *Phys. Rev. Lett.* **2009**, *102*,

164502-1-4.

- (2) de Gans, B.; Duinevald, P.C.; Schubert, U.S. Inkjet Printing of Polymers: State of the Art and Future developments *Adv. Mater.* **2004** *16*, 203-213.
- (3) Bartolo, D.; Boudaoud, A.; Narcy, G.; Bonn, D. Dynamics of Non-Newtonian Droplets *Phys. Rev. Lett.* **2007**, *99*, 174502-1-4.
- (4) Bergeron, V.; Bonn, D.; Martin, J.Y.; Vovelle L. Controlling droplet deposition with polymer additives *Nature* **2000**, *405* 772-775.
- (5) Yarin, A.L. DROP IMPACT DYNAMICS: Splashing, Spreading, Receding, Bouncing *Annu. Rev. Fluid. Mech.* **2006**, *38* 159-92.
- (6) Leichle, T.; Tanguy, L.; Nicu, L. Electrowetting-assisted drop deposition for controlled spotting *Appl. Phys. Letts.* **2007**, *91*, 2241021-3.
- (7) Zang, D.; Wang, X.; Geng,X.; Zhang,Y.; Chen,Y. Impact dynamics of droplets with silica nanoparticles and polymer additives *Soft matter* **2013**, *9*, 394-400.
- (8) Ayatouna, M.; Bartolo, D.; Werdman, G.; Bonn, D.; Rafai, S. Impact dynamics of surfactant laden drops: dynamic surface tension effects *Exp. Fluids* **2010**, *48* 49-57.
- (9) Smith, M.I.; Bertola, V. Effect of Polymer Additives on the Wetting of Impacting Droplets *Phys Rev Letts* **2010**, *104* 154502-1-4.
- (10) Bertola, V. Dynamic wetting of dilute polymer solutions: The case of impacting droplets *Adv. Coll. Int. Sci.* **2013**, *193* 1-11.
- (11) Smith, M.I.; Bertola, V. Particle velocimetry inside Newtonian and non-Newtonian droplets impacting a hydrophobic surface *Expts in Fluids* **2011**, *50* 1385-1391.
- (12) Rozkhov, A.; Prunet-Foch, B.; Vignes-Adler, M. Impact of drops of polymer solutions on small targets *Phys. Fluids* **2003**, *15*, 2006-2019.

- (13) Bertola, V. An experimental study of bouncing Leidenfrost drops: Comparison between Newtonian and viscoelastic liquids *Int. J. Heat Mass Transfer* **2009**, *52*, 1786-1793.
- (14) del Rio, O.I.; Neumann, A.W. Axisymmetric Drop Shape Analysis: Computational Methods for the Measurement of Interfacial Properties from the Shape and Dimensions of Pendant and Sessile Drops *J. Colloid Int. Sci.* **1997**, *196*, 136-147.
- (15) Blake, T.D. The physics of moving wetting lines *J. Colloid Int. Sci.* **2006**, *299*, 1-13.
- (16) Bonn, D.; Eggers, J.; Indekeu, J.; Meunier, J.; Rolley, E. Wetting and spreading *Rev. Mod. Phys.* **2009**, *81*, 739-805.
- (17) Eral, H.B.; 't Mannetje, D.J.C.M.; Oh, J.M. Contact angle hysteresis: a review of fundamentals and applications *Colloid Polym. Sci.* **2013**, *291*, 247-260.
- (18) de Gennes, P.G. Wetting: statics and dynamics *Rev. Mod. Phys.* **1985**, *57*, 827-863.
- (19) Bartolo, D.; Josserand, C.; Bonn, D. Retraction dynamics of aqueous drops upon impact on non-wetting surfaces *J. Fluid Mech.* **2005**, *545*, 329-338.

## Figures

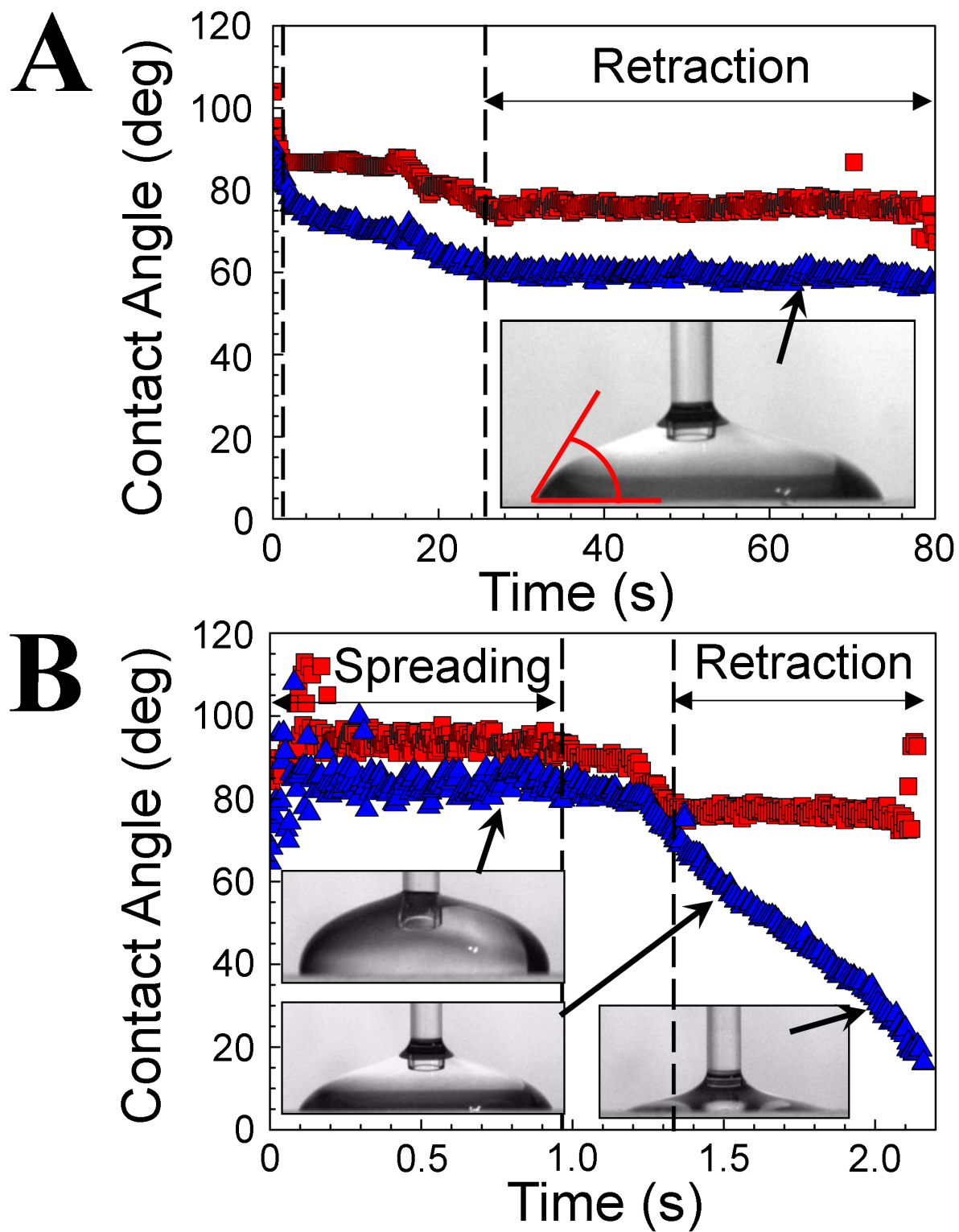


Figure 1: Syringe driven flows of water and PEO solution drops. The contact angle measurements for spreading at  $485 \mu\text{ls}^{-1}$  and retraction of drops of water ( $\square$ ) and  $200 \mu\text{gml}^{-1}$  PEO ( $\triangle$ ). Retraction flow rate is A)  $6 \mu\text{ls}^{-1}$ . B)  $485 \mu\text{ls}^{-1}$ .

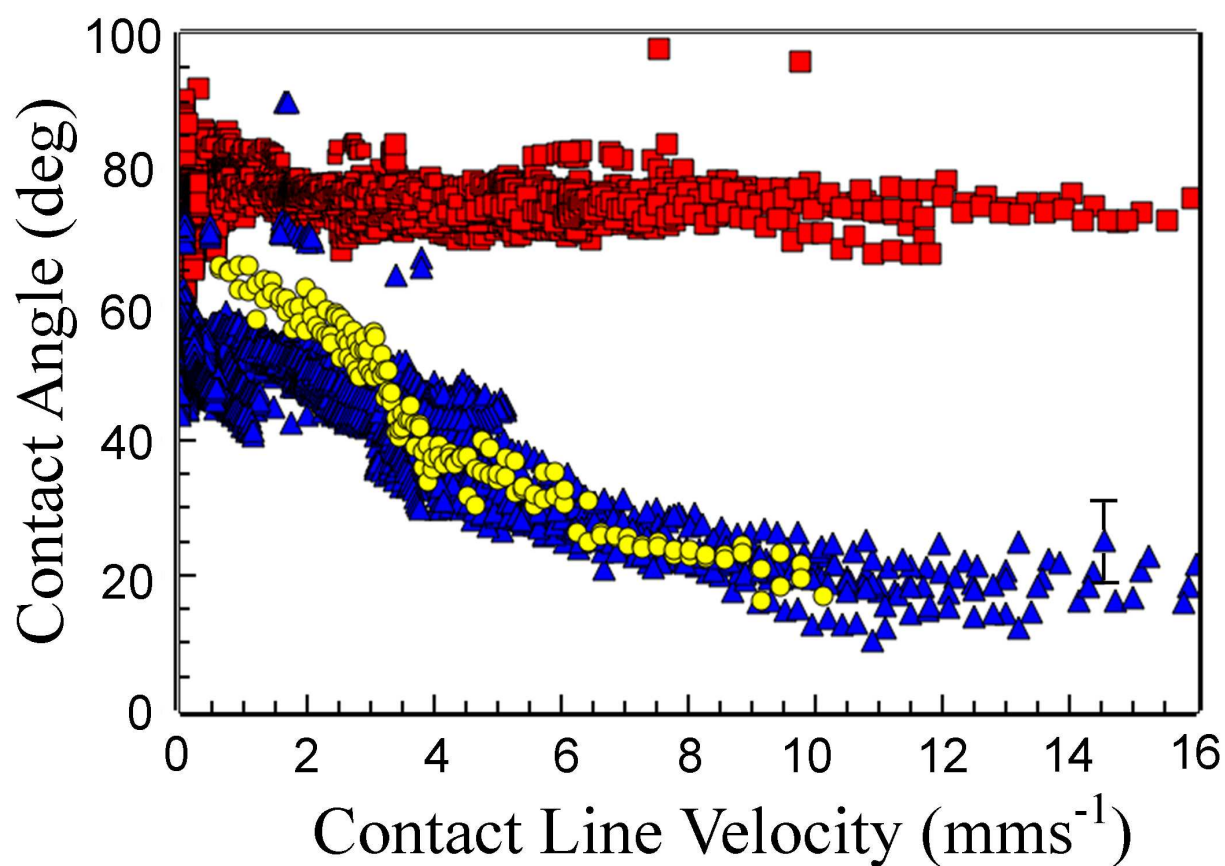


Figure 2: Contact angle dependence on contact line velocity. The contact angle during the retraction phase of drops of water (□) and 200  $\mu\text{gml}^{-1}$  PEO solution (△) on a polystyrene surface. The changes in the PEO solution drops' contact angle indicates a resistive force that increases with velocity. Also shown is data for a two stage experiment. Droplets of water were retracted on a surface upon which a PEO drop had previously been retracted (○)

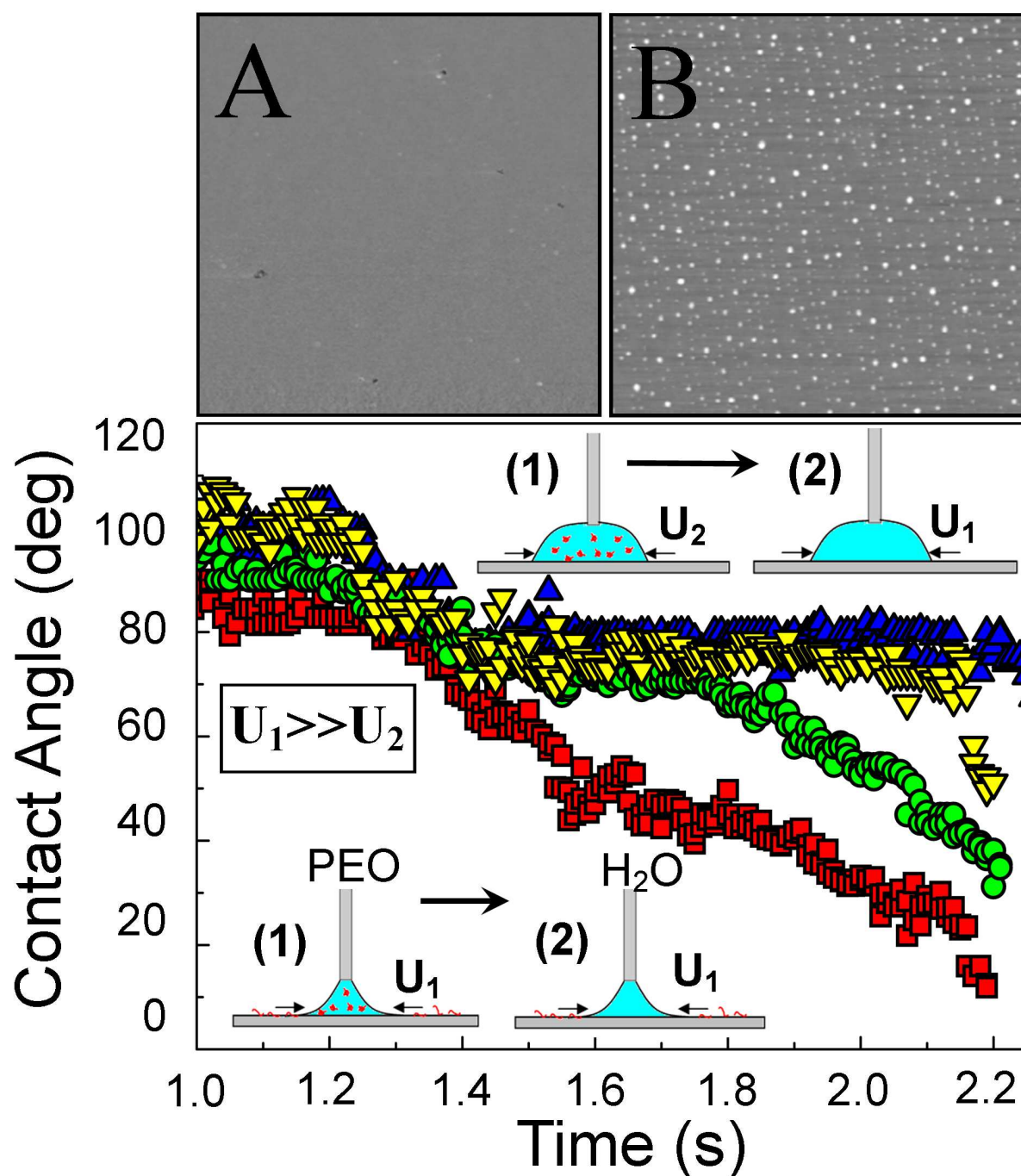


Figure 3: The deposition of polymer during contact line retraction. Top) AFM phase images ( $10 \times 10 \mu\text{m}$ ) were taken after a  $200 \mu\text{gml}^{-1}$  PEO drop was spread and then retracted at flow rates of A) 6 and B)  $485 \mu\text{ls}^{-1}$ . Bottom) A two stage experiment. Stage 1: Drops of  $200 \mu\text{gml}^{-1}$  PEO were spread and retracted at different flow rates. Stage 2: pure water drops were spread and retracted at a flow rate of  $485 \mu\text{ls}^{-1}$  at the same location. The figure shows the contact angles during retraction of these water drops. The PEO drops used to prepare the surfaces were retracted at flow rates of  $485$  ( $\square$ ),  $278$  ( $\circ$ ),  $56$  ( $\nabla$ ) and  $6 \mu\text{ls}^{-1}$  ( $\triangle$ ). The difference in behaviour is indicative of different amounts of polymer being deposited at the interface.

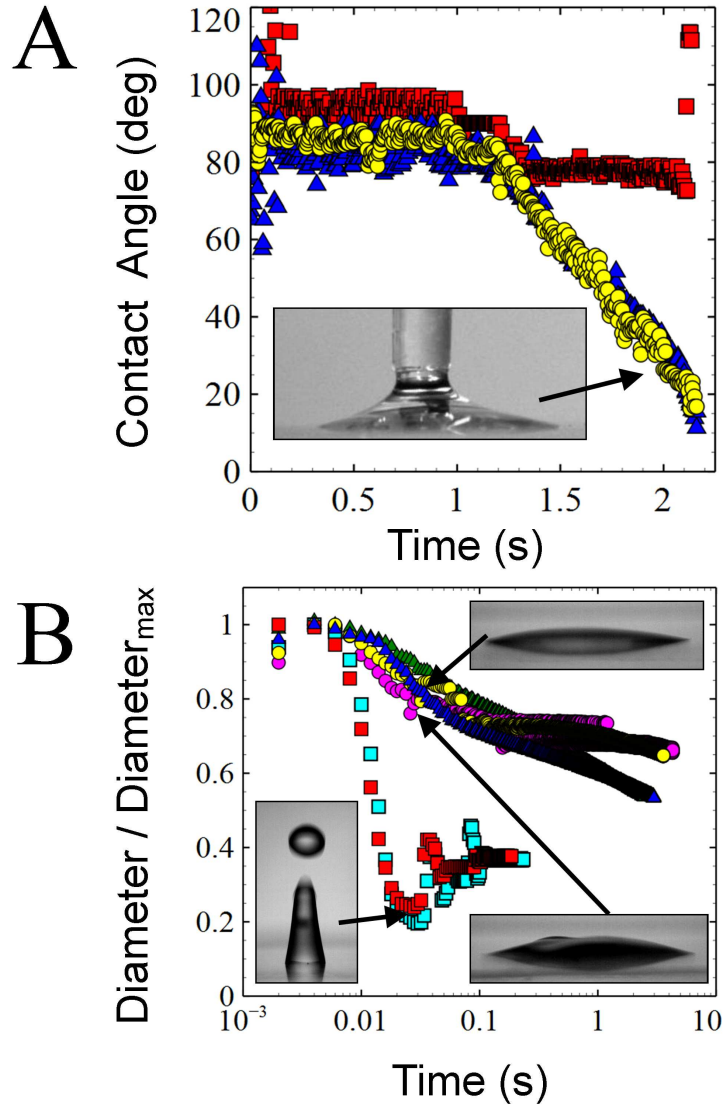


Figure 4: Role of pre-deposited polymer in dissipation at the contact line. A) A comparison of the contact line dynamics for syringe driven flows. Three types of droplet are shown spreading and retracting at  $485 \mu\text{ls}^{-1}$ . A water drop on a PS surface ( $\square$ ), a  $200 \mu\text{gml}^{-1}$  PEO drop on a PS surface ( $\triangle$ ) and a two stage experiment in which the data shows a water drop retracting on a PS surface upon which a PEO drop had been previously spread and retracted ( $\circ$ ). B) A comparison of the dynamics for the same three types of experiment performed using drop impact.(Color online)



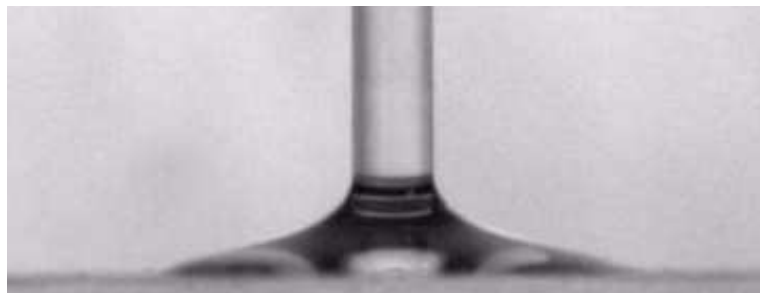


Figure 5: Table of Contents Graphic