Effect of Polymer Additives on the Wetting of Impacting Droplets

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When a droplet of water impacts a hydrophobic surface, the drop is often observed to bounce. However, for about 10 years it has been known that the addition of very small quantities (~ 100 ppm) of a flexible polymer such as poly-(ethylene oxide) can completely prevent rebound. This effect has for some time been explained in terms of the stretching of polymer chains by a velocity gradient in the fluid, resulting in a transient increase in the so-called "extensional viscosity." Here we show, by measuring the fluid velocity inside the impacting drop, that the extensional viscosity plays no role in the antirebound phenomenon. Using fluorescently labeled λ DNA we demonstrate that the observed effect is due to the stretching of polymer molecules as the droplet edge sweeps the substrate, retarding the movement of the receding contact line.

Droplet impact phenomena have intrigued scientists for over a century [1]. With Edgerton's invention of a stroboscopic photography technique, impact dynamics of drops could be carefully visualized for the first time [1]. The more recent development of high speed cameras has enabled a large research effort to characterize drop impact phenomena under a wide range of conditions [1]. Controlling droplet deposition is of tremendous commercial interest. The ecological and economic benefits to the agrochemical industry in limiting wasted pesticides are enormous [2], but inkjet printing and many spray applications, including spray cooling, also require careful control of the droplet impact [3], making suppression of droplet rebound an important industrial problem.

When a drop of water impacts a surface, inertia causes it to spread out into a disc shaped "lamella." Subsequently, surface tension causes the drop to retract. On hydrophobic surfaces, such as the waxy leaf of a plant, if insufficient energy has been dissipated (largely due to viscous forces within the fluid) the drop will then bounce off the surface. However, adding small quantities (~ 100 ppm, 1 ppm $=$ 1 μg/ml) of a flexible polymer such as poly-(ethylene oxide) (PEO) completely alters the impact dynamics with the rebound of droplets completely suppressed. This is surprising since the shear viscosity and surface tension of such drops are almost identical to those of pure water. Under a strong elongational flow (where the fluid element is deformed in the direction of travel rather than sheared), a polymer undergoes an abrupt transition from a random coil to a stretched out state [4]. A droplet spreading on a surface exhibits 2D elongational flow with axial symmetry, which led to the proposal that dissolved polymers might stretch, producing an increase in the macroscopically observed extensional viscosity. Since their discovery, the antirebound properties of dilute polymer solutions have thus

been attributed to dissipation by the transient increase in viscosity [5].

Subsequently, several difficulties with this interpretation have been discovered. First, an increased extensional viscosity should affect both the spreading and subsequent retraction of the drop on the surface. However, only drop retraction is affected, with the maximum spreading diameter of both PEO and pure water drops being similar [5–7]. Second, if interfacial effects are removed, by impact on heated surfaces or small targets [8,9], the antirebound phenomenon is no longer effective, thus pointing to a significant role for the liquid-solid interface.

Our experimental results enable us to exclude the extensional viscosity as a significant factor during the retraction phase and suggest an alternative mechanism for the rebound suppression. This is achieved by analyzing the fluid velocity inside the spreading and retracting drop using fluorescent particles, and then directly observing the contact line using fluorescently labeled λ-DNA.

Experimental setup.—Droplets were formed at the end of a blunt hypodermic needle (18 G, Drop diameter: water $= 2.76 \pm 0.14$ mm, PEO $= 2.66 \pm 0.1$ mm), suspended from a micrometer adjusted mount. Our system is constructed around an inverted epifluorescent microscope containing a x40 objective (NA 0.75) and filter set (No. 18/9, Zeiss). Excitation is provided by a pulsed uv laser ($\lambda \sim 355$ nm, repetition rate ~ 8 kHz) for the particle velocimetry measurements and a visible continuous wave laser ($\lambda \sim 450$ nm) for the DNA experiments. The microscope is equipped with a high speed CMOS camera (Phantom v9.1) fitted with an image intensifier (Lambert Instruments). The falling droplet passes through a light gate triggering the collection of a series of images. Experiments were performed on glass coverslips coated with a thin film of Fluropel (Cytonix, contact angle

$\sim 106°$). 2 μm fluorescent colloids were diluted with the appropriate solution (water or 200 ppm PEO) to a final concentration of <0.001 wt %. Movies for particle velocimetry were collected at 2000 fps ($f_{Laser} \sim 8$ kHz) resulting in each colloid being exposed 4 times in each frame [see inset of Fig. 1(b)]. During spreading, particles were observed to follow radial paths. A linear fit to each sequence of particles was extrapolated back to the point of intersection with a reasonable error, to estimate the position of the drop center and corresponding radial distance of each particle. The time (measured relative to the trigger point) and velocity ($V_{Colloid} \sim \Delta x f_{Laser}$) were also measured.

Figure 1 shows a comparison of the velocities as a function of time inside droplets of pure water [Fig. 1(a)] and 200 ppm PEO solution [Fig. 1(b)] at different radial positions (drop height 100 mm, impact velocity ~ 1400 mm s^{-1}). Using these plots, we can estimate the initial retraction velocity of the fluid for water and PEO

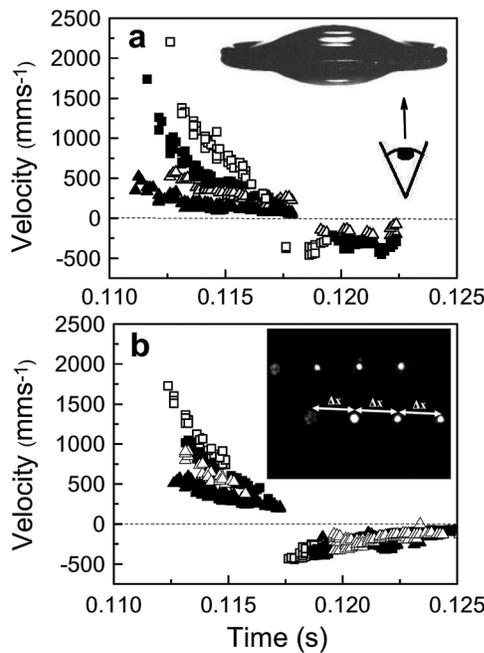FIG. 1.　Particle image velocimetry. Example data sets showing the fluid velocity as a function of time for (a) pure water [at radii (mm) 0.7 ▲, 1.3 △, 1.6 ■, 2.8 □] (b) 200 ppm PEO (at radii 1.2 ▲, 2.0 △, 2.1 ■, 2.7 □). The radius of the contact line at maximum spread for water = 4.1, PEO = 3.9 mm. Inset (a) shows a spreading droplet. The arrow indicates the view obtained by the microscope objective. Inset (b) shows a typical image obtained of fluorescent colloids in a spreading drop. Using particle image velocimetry the initial retraction velocity of the fluid as a function of radius can be estimated. Images are collected at 2000 fps but the laser produces 8000 pulses/s. This results in each particle being exposed 4 times. By measuring the distance traveled by each particle between pulses the velocity of the fluid can be estimated ($V_{Colloid} \sim \Delta x f_{Laser}$). The direction of fluid motion in the PIV inset is from left to right.

drops as a function of the radial position (Fig. 2). Surprisingly, there is negligible difference between the two fluids.

When a drop reaches maximum spreading, the elastic energy due to deformation of the surface causes the drop to retract. The speed of the retraction is determined by the amount of stored interfacial energy and the viscosity of the fluid [6]. Consequently, if the two drops, which have similar spreading radii, retract at the same speed, the extensional viscosities must also be similar. For comparison, the retraction velocity of the contact line taken from macroscopic movies is also included. The PEO drop edge, by contrast to the bulk of the fluid, is found to retract an order of magnitude more slowly than that of pure water. Since the current understanding of the phenomenon relies on an increase in the extensional viscosity of the retracting drop, this cannot be a correct picture of the physical mechanism. Our data rather suggest that the reduction in retraction velocity happens initially at the drop edge, leading to a gradual reduction in velocity in the drop interior [Fig. 1(b)]. As can be seen in the supplementary video 1 in [10], the motion of the fluid inside the drop even reverses direction, with the fluid alternately moving away and towards the retreating contact line, providing further evidence that it is the contact line and not an increased viscosity that affects the dynamics of the drop.

To confirm that the antirebound phenomenon is due to dissipation at the contact line we examine the effect of polymer concentration on the retraction of the contact line.
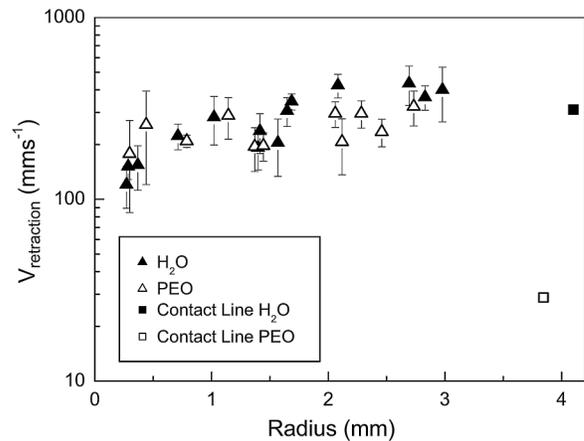

FIG. 2.　Initial retraction velocities in a droplet. Initial retraction velocities as a function of radial position inside pure water (▲) and 200 ppm PEO drops (△) as compared with the drop edge for water (■) and 200 ppm PEO drop (□). The retraction velocity for the drop edge in a PEO drop is an order of magnitude slower than in the bulk of the drop. Since the initial retraction velocities of the bulk fluid are similar for both water and PEO the extensional viscosities must also be similar. The antirebound effect cannot therefore be due to an increase in extensional viscosity, rather it appears to be the drop edge which slows retraction.

Using a Phantom V9.1 CMOS high speed camera, fitted
with a zoom lens, high speed, high magnification movies of
PEO drops falling from 20 mm were collected (supple-
mentary video 2 [11]). Movies were collected at 5000 fps
(800 × 400 pixels) of the contact line of droplets during
spreading and retraction. MATLAB software was then used
to extract contact angles and the position of the drop edge.
Careful observation of these movies provides additional
evidence that the antirebound phenomenon is a result of
contact line dissipation rather than changes in the drop's
extensional viscosity. Upon reaching maximum spreading
stored interfacial energy drives retraction of a droplet.
During the initial stage of retraction, the bulk of the drop's
fluid moves towards the center of the drop. The inertia of
this fluid movement produces a force on the contact line.
For a pure water drop there is little or no resistance to
movement at the drop edge and hence the drop retracts
quickly and with sufficient energy that it may rebound
from the surface (inset Fig. 3). A similar initial movement
of the bulk fluid is observed for a PEO drop, however, in
this case the contact line seems to resist the fluid move-
ment. The inertia of the bulk fluid causes the contact line to
move, but sufficient resistance occurs that there is insuffi-
cient energy for the drop to rebound. What follows is a
series of oscillations in the drop in which the contact line

moves intermittently (supplementary video 2 [11] and inset
of Fig. 3). The distance moved by the contact line during
the first oscillation (X_{slip}) therefore represents a measure of
the dissipation at the contact line. For each polymer con-
centration the drop edge's initial slip distance was calcu-
lated from an average of 8 drops. The first slip length is
found to scale with polymer concentration up to some
saturation value (Fig. 3), implying increasing dissipation
at the contact line as the number of molecules present
increases.

To probe the details of this edge effect, we prepared a
solution of 200 ppm PEO to which we added λ-DNA
(0.2 ppm λ-DNA (NEB), stained with YOYO-1 dye
(Invitrogen) at a dye:bp ratio of 1:8, dissolved in a solution
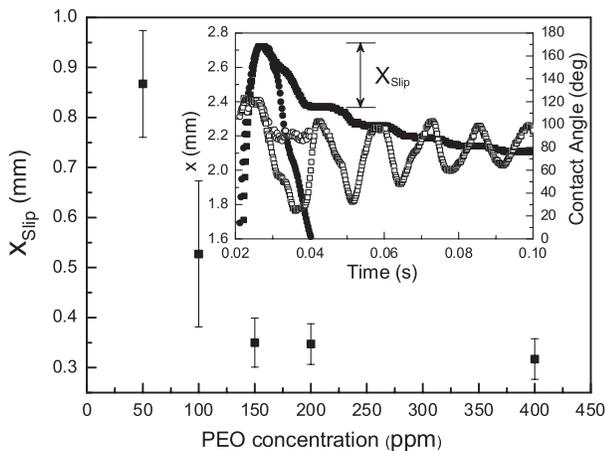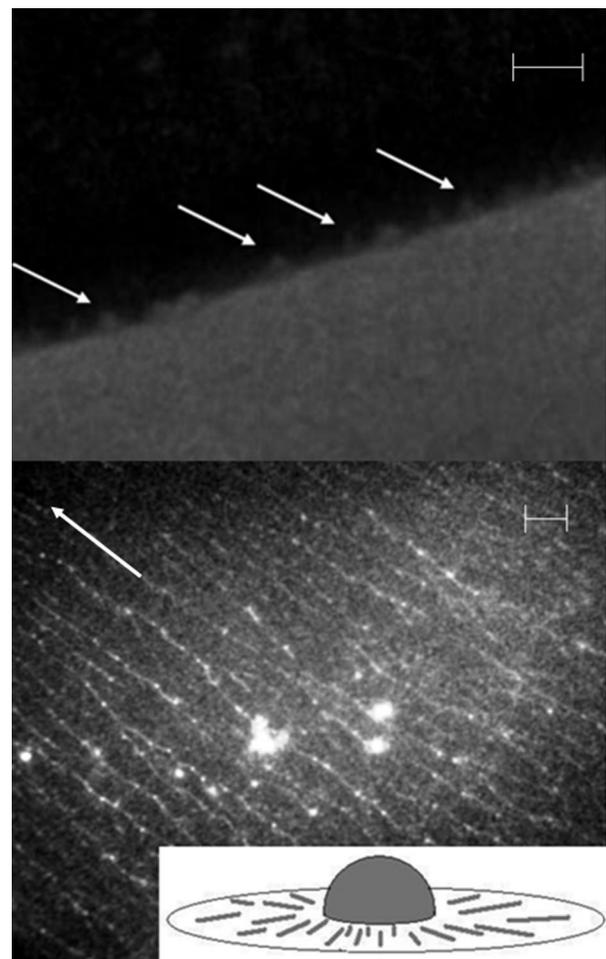of 200 ppm PEO.). Movies of DNA solutions were col-

FIG. 3. Slip distance of the droplet edge. Inset: The position of
the drop edge (closed symbols) and corresponding contact angle
(open symbols) for an impacting drop of water (○) and 200 ppm
PEO (□), drop height 20 mm. Main Panel: Distance travelled by
the contact line during the first oscillation of the retracting drop
for different concentrations of PEO. For PEO drops it is observed
that the majority of the fluid oscillates towards and away from
the drop edge resisted by a force at the contact line. The inertia
of the moving fluid causes the contact line to move with every
oscillation, a distance which depends on polymer concentration.
The distance moved during the first oscillation is indicated by the
value X_{slip}. A higher concentration of polymer results in a
stronger resistance to movement at the contact line, providing
additional evidence that the antirebound phenomenon is a con-
tact line effect.

FIG. 4. Stretching of DNA by retracting droplets. (Top) Close-
up of receding drop edge showing "DNA fingers" protruding
beyond the contact line. (Bottom) Fluorescent microscope image
of DNA, which is left behind on the surface after the droplet has
retracted. The molecules are aligned radially (see inset). The
arrow indicates the direction of the retreating contact line. The
scale bar in both images is 20 μm which is comparable to the
length of a single stretched molecule. The image shows multiple
DNA molecules lying end to end.

lected at a frame rate of 1000 fps with an exposure time of 400 μs. λ-DNA is a linear biopolymer which adopts a random coil conformation, ~ 1.4 μm diameter [12], although its stretched length is ~ 22 μm [12] and thus visible using a fluorescent microscope (Experiments using 10 ppm λ-DNA in water confirmed that DNA, like PEO, is capable of suppressing the rebound of droplets, although at such low wt % concentrations the retraction velocity of the DNA drops is significantly higher). Using a drop height of 20 mm and focusing about 2/3 of the way to the maximum spreading radius, the retraction of a droplet was observed [Fig. 4(a) and supplementary video 3 [13]). The moving contact line shows thin "fingers" extending from the contact line which persist for several frames at a time before disappearing. The fingers fluoresce brightly and are of comparable size to stretched λ-DNA molecules. After the passing of the contact line, radially oriented DNA can be observed on the substrate, bearing strong similarities to that often seen during molecular combing [14,15] [Fig. 4(b)].

At this stage we propose a tentative model. As the drop edge sweeps the substrate, molecules at the contact line are stretched in a manner similar to other DNA stretching methods such as molecular combing or air blowing techniques [15]. Factors such as the entropic resistance to extension and the hydrodynamic drag of water molecules associated with the polymer chains resist the retraction, slowing the motion of the drop edge. We might understand this as an "effective friction" of the contact line.

In conclusion, our work clearly demonstrates that a transient increase in the extensional viscosity of dilute polymer solutions is not responsible for the drop antirebound phenomenon. By directly visualizing the retracting drop edge, and the substrate afterwards, we showed that the stretching of λ-DNA, and by analogy PEO or any other flexible polymer chain, produces an effective resistance to the motion of the contact line. This prevents droplets from bouncing on a hydrophobic surface.

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[11] See supplementary material at http://link.aps.org/supplemental/10.1103/PhysRevLett.104.154502 for retracting drop (200 ppm, 5000 fps)
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