VELOCITY MEASUREMENTS INSIDE IMPACTING DROPS OF DILUTE POLYMER SOLUTIONS

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ABSTRACT
A particle tracking measurement technique is used to measure the velocity field inside impacting drops, both of pure water and of aqueous solutions of 200ppm poly-(ethylene oxide) (PEO). Dilute solutions of PEO have been known for some time to suppress the rebound of water from hydrophobic surfaces. The dissipation has traditionally been attributed to an increased extensional viscosity as the polymers stretch in the extensional flow of the droplet. Our results enable us to infer that the extensional viscosity of PEO drops, during both the spreading and retraction phase, is similar to that of pure water. These data, in combination with macroscopic measurements of the apparent dynamic contact angle, suggest that the true source of dissipation lies at the droplet edge.

INTRODUCTION

Liquid drops may contain macromolecular additives for various reasons. In some cases, additives are active substances (for example, cleaning agents) which must be deposited on a target surface by means of a spray. In other cases, additives have the specific purpose of changing the fluid properties in order to affect the drop impact morphology: for instance, thickening agents increase the fluid viscosity hence reduce the maximum spreading diameter of the drop upon impact [1].

Flexible polymers, i.e. those polymers characterized by a high molecular mass and a low degree of branching, represent an interesting class of additives, because they can change significantly the morphology of drop impact, both on homo-thermal and on heated surfaces. In particular, it is known that these additives can completely inhibit drop bouncing on hydrophobic surfaces [2,3], change the critical conditions for drop break-up upon impact (splashing threshold) [4,5], and suppress secondary atomization observed when drop impact on hot surfaces, which affects the definition of dynamic Leidenfrost temperature [5,6].

Among these effects, suppression of drop bouncing (anti-rebound effect) has a high industrial relevance, because it can improve several spray applications, including distribution of agrochemicals and as drug delivery [2,3,7]. Thus, in order to achieve maximum benefits in these applications, it is important to know the actual physical mechanism of the phenomenon.

Initially, this effect was explained in terms of the stretching of polymer chains by a velocity gradient in the fluid [8], resulting in a transient increase in the so-called "extensional viscosity" (the ratio of the first normal stress difference to the rate of elongation of the fluid), which for a polymer solution can be two or three orders of magnitude higher than that of the solvent. In particular, it was suggested that the elongational viscosity causes large energy dissipations during drop spreading immediately after impact on the target surface, so that nothing of the impact kinetic energy is available to propel the drop off the surface itself [2-4].

This seemed to be confirmed by measurements of the retraction velocity of the liquid after maximum spreading, which for polymer solutions is about one order of magnitude smaller than that measured for the pure solvent [4,5], and by experimental evidence of a strong correlation between the anti-rebound effect and the fluid elongational viscosity [7,9].

However, further investigations have demonstrated that in the absence of direct contact between the liquid and the substrate, the anti-rebound effect is no longer observed. A study of drops impacting on small targets [10] suggests that polymer additives do not change the retraction velocity, while independent experiments on Leidenfrost drops (where the liquid is separated from the target surface by a thin vapor layer) [11,12] show that they cause only a slight reduction.

Because in these experiments wetting effects are absent or negligible, one must conclude that the retraction velocity reduction observed in drops containing flexible polymers impacting on solid surfaces is due to the drop-surface interaction rather than to an increased energy dissipation connected to the elongational viscosity of the fluid.

Furthermore, measurements of the maximum bouncing height of Leidenfrost drops (indicative of the fraction of the initial kinetic energy which is not dissipated during impact) suggest that in some conditions polymer additives reduce instead of increasing the overall energy dissipation and enhance instead of suppressing bouncing [11,12]. Therefore, one must conclude that the real cause of this phenomenon is to be sought in the dynamic wetting behaviour of dilute polymer

solutions, and not in some bulk property of the fluid such as the elongational viscosity.

To shed more light on the actual roles of both elongational viscosity and wetting in the anti-rebound phenomenon, this paper presents particle tracking velocimetry measurements of the velocity field inside the impacting drop, and compares them with macroscopic measurements obtained by high-speed imaging [13,14].

Results show that whilst the contact line receding velocity is one order of magnitude slower for drops containing polymer additives compared with drops of pure water, the velocity fields measured inside drops are similar. This rules out any transient changes of the fluid bulk properties, including elongational viscosity. Moreover, dynamic contact angle measurements combined with direct visualisation of fluorescent biopolymer molecules suggest that the true cause of the anti-rebound effect is the change in the dynamic wetting behaviour of droplets, induced by localised polymer molecules stretching at the contact line.

EXPERIMENTS

Materials

PEO drops were created from a 200 ppm solution in de-ionized water. The PEO, supplied by Aldrich Chemicals in the form of granular powder, had an average molecular weight of 4,000,000 a.m.u. and a typical density of 1210 kg/m^3. The solution was prepared by gently dissolving the polymer into a batch of de-ionised water, then mixed for about one hour using a magnetic stirrer.

The equilibrium surface energy of the polymer solution, measured using a maximum bubble pressure in-strument (Krüss PocketDyne), was 69 mJ/m^2, while shear viscosity, measured with a rotational rheometer (Haake MARS II) equipped with a 60 mm plane/plane geometry and Peltier temperature controller, was 1.23 mPa·s.
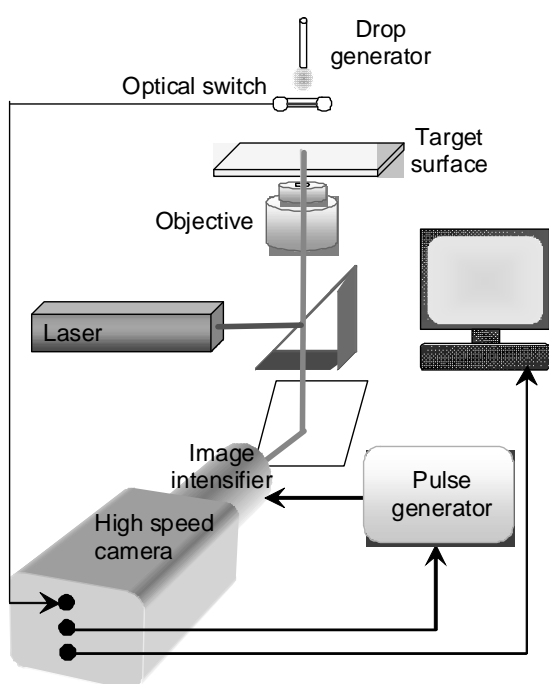

Figure 1. Schematic description of the experimental setup used for particle tracking velocimetro.

The target surface used in all experiments was a glass slide coated with Fluoropel PFC1302A (Cytonix Corp.), a 2% fluoropolymer solution in low boiling point (135°C) fluorosolvent, with equilibrium contact angles of about 105°. The Fluoropel coating was created by dipping glass slides into the liquid, and then dried at 90°C for 10 minutes to optimize adhesion.

Experimental setup and procedure

Droplets were formed at the end of a blunt hypodermic needle, suspended from a micrometer-adjusted mount, which allowed changing the falling height hence the impact Weber number. The experimental setup used for particle tracking, shown schematically in Figure 1, was built around an inverted epi-fluorescent microscope containing a x40 objective (NA 0.75) and filter set. Excitation was provided by a pulsed UV laser (λ ~ 355nm, repetition rate ~ 8kHz). The microscope was equipped with a high speed camera (Phantom v9.1) fitted with image intensifier (Lambert Instruments). The falling droplet passed through a light gate triggering collection of a series of images.

For macroscopic measurements (i.e., drop base diameter and contact angles), a 0.838 mm i.d. needle (gauge 18) was placed 185 mm above the target surface. The theoretical free-fall velocity was 1.9 m/s, corresponding to an impact Weber number of about 170 for both water and the polymer solution. Impacts were recorded by a Mikrotron MC1310 camera equipped with a 18–108/2.5 lens (Navitar Zoom 7000) and horizontally aligned with the target surface. Back-to-front illumination was provided by a low-power (2 W) LED backlight (Philips AccentLED) to avoid unwanted heating.

For particle tracking experiments, 2μm fluorescent colloids were diluted with the appropriate solution (de-ionised water or a 200 ppm PEO solution) to a final concentration of <0.001wt%. Drops were released from a height of 100 mm, corresponding to an impact velocity of about 1.4 m/s. Movies for particle velocimetry were collected at 2000 fps (fLaser ~ 8kHz) resulting in each colloid being exposed four times in each frame, as shown in Figure 2. 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 centre and corresponding radial distance of each particle. Time was measured relative to the trigger point, and velocity at each radial position (Eulerian approach) was calculated as $V_P = f_{laser}\Delta x$.
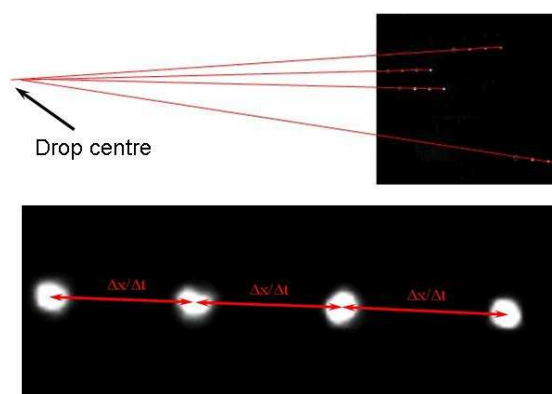

Figure 2. Measurement of the fluid velocity inside the impacting drop by particle tracking.

For macroscopic measurements, images with a resolution of 960×200 pixels were captured at 2500 frames per second. Magnification was kept constant throughout all experiments and lengths on the image could be calculated by comparison with a reference length (typical spatial resolution: 50 pixels/mm). Quantitative data were extracted from images using proprietary software developed in LabView and Matlab environments, which after background subtraction and image optimization measured the base diameter of drops, as well as the left and right contact angles using the drop profile tangent method.

RESULTS

From particle tracking measurements, one could obtain the fluid velocity inside the impacting drop at different radial positions during inertial spreading and receding. Velocities measured inside droplets of pure water and droplets of 200 ppm PEO solution are shown in Figure 3 and Figure 4, respectively. From these plots, one can see that the magnitudes of fluid velocity at different times are almost identical for the two drops, irrespective of the presence of the polymer additive. This is also true for velocity gradients, which are plotted with respect to time in Figure 5 for the two fluids considered.

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 [9]. Consequently, if the two drops, which have similar spreading radii, retract at the same speed, and with the same velocity gradient, the extensional viscosities must also be similar.

However, this is no longer true for the retraction velocity of the contact line as can be measured from macroscopic movies. The difference in the retraction velocity of the drop edge can be obtained by tracking the variation in time of the dimensionless base diameter, as shown in Figure 6 (where the origin of time is the instant of maximum radial spreading, and with an apparent contact angle of 90°).

For drops containing the polymer additive, the time required for the base diameter to reach the final equilibrium value is one order of magnitude longer than for drops of pure water. As a consequence 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.

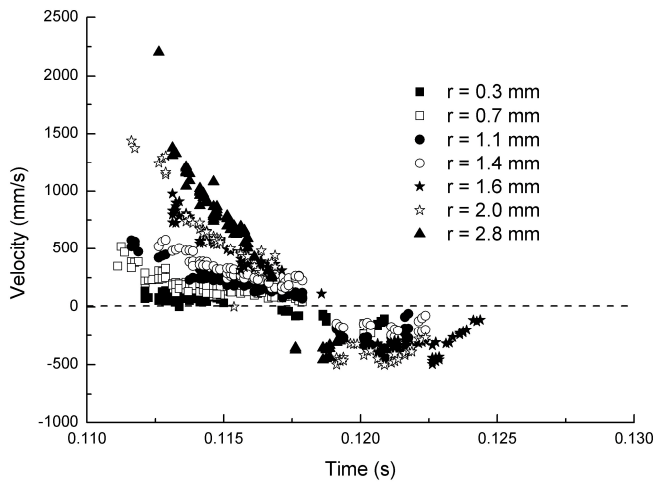Figure 5. Velocity gradient of the fluid inside impacting drops during spreading.

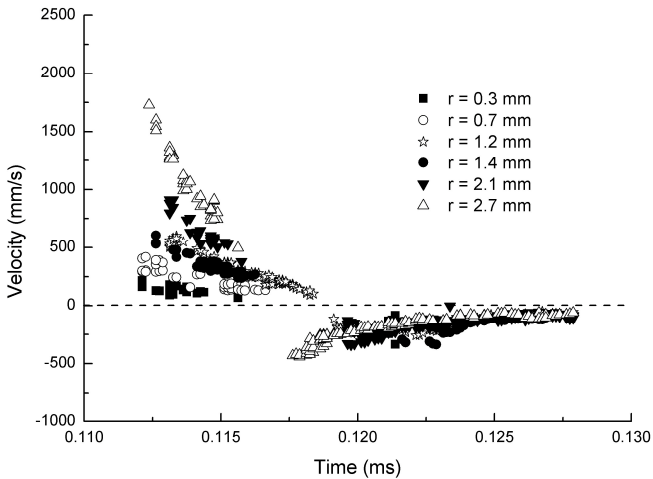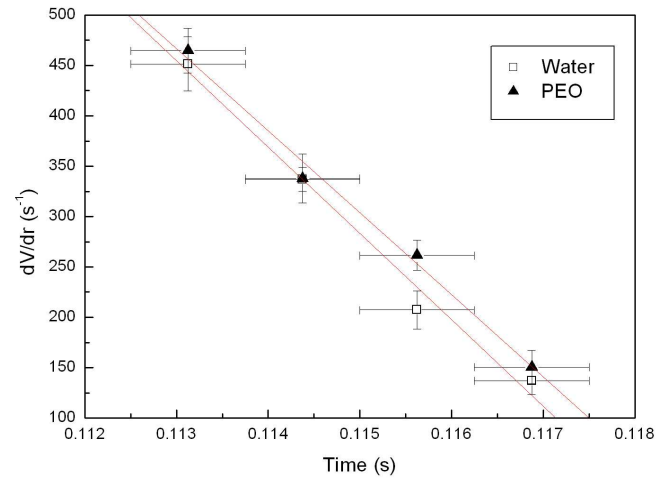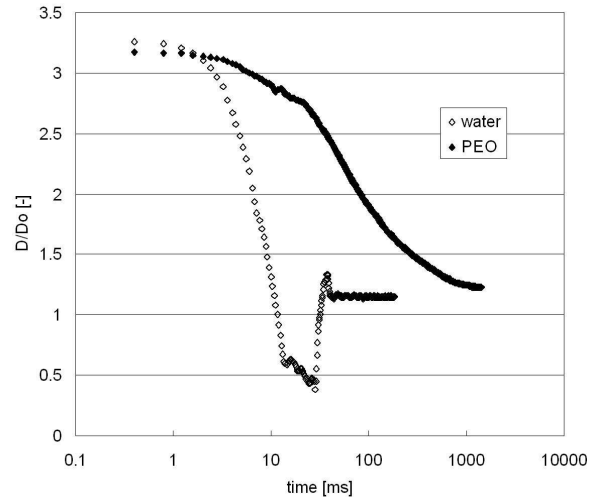Figure 3. Radial velocity measured in a water drop at different distances from the spreading drop centre.

Figure 4. Radial velocity measured in a drop of PEO solution, at different distances from the spreading drop centre.

Figure 6. Drop diameter during the retraction stage, normalised with respect to the equilibrium diameter, D_0.

Contact angle measurements, shown in Figure 7, provide a better insight of the phenomenon. Between the end of expansion and the beginning of retraction, the radial velocity is zero (i.e., the apparent contact line does not move) and the contact angle value changes from advancing (> 90°) to receding (< 90°) in a very short time (few milliseconds). Note that such contact angle hysteresis is in principle different from the one usually discussed in the literature [15], which can be observed when the contact line oscillates about its stable equilibrium position (minimum energy). In this case, the contact angle hysteresis is about an unstable equilibrium position, i.e. about a local surface energy maximum. A naïve interpretation of this phenomenon can be given in terms of the Young-Laplace force balance: the contact angle reduces until the horizontal component of the liquid-vapour interfacial force is large enough to initiate retraction.

While drops of pure water initiate retraction when the contact angle has reached a value around 30º, as shown in Figure 7, for drops containing the additive retraction begins only when the dynamic contact angle is very small. This suggests that the horizontal component of the driving force required to initiate the movement of the contact line is much larger than in the case of pure water, as if the contact line was pinned on the surface, or encountered some form of frictional resistance.

Since both drops of pure water and those of polymer solution impact on identical surfaces, the difference observed in the contact angle hysteresis cannot be interpreted in terms of surface roughness or chemical heterogeneity. Thus, the only options available are: (i) the polymer additive changes the chemical structure of the surface, (ii) it changes the properties of the liquid film left behind the contact line as the drop edge sweeps the surface.

Recently, it has been demonstrated that liquid droplets containing a fluorescent biopolymer (λ-DNA) impacting on a hydrophobic surface leave stretched polymer molecules deposited on the target surface in a direction perpendicular to the receding contact line [13]. This phenomenon, which bears strong analogies with various well-known DNA stretching techniques, such as molecular combing and air-blowing [16], is likely to be due to the synergetic action of hydrodynamic and interfacial forces exerted on DNA molecules as the receding meniscus sweeps the surface.
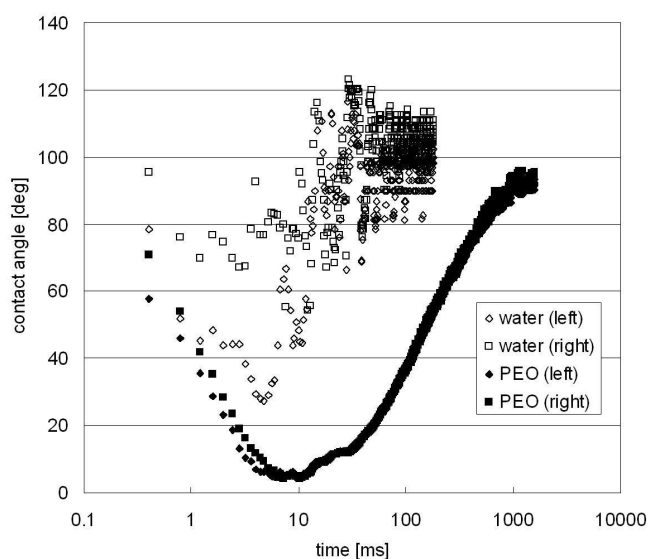
These results suggest that the contact line retardation observed during the retraction of drops of polymer solutions as compared with drops of the pure solvent is caused by the polymer molecules stretching occurring when the receding contact line sweeps the impact surface. This can be interpreted, from a macroscopic point of view, as an additional, dissipative force acting on the contact line and opposed to its movement, or contact line friction, which affects both the contact line retraction velocity and the apparent dynamic contact angle

CONCLUSIONS

Particle tracking velocimetry measurements of the local fluid velocity inside impacting drops show that polymer additives do not have appreciable effects on the velocity field, in particular during the retraction stage after maximum spreading. On the contrary, the recoil velocity of the contact line only is one order of magnitude smaller for the polymer solution drop, which prevents drop bouncing on hydrophobic surfaces. These results show that the bulk properties of the fluid, such as the elongational viscosity, do not have a significant role in preventing drop rebound.

Measurements of the apparent contact angle showed that in drops of PEO solution this quantity is much smaller than in drops of pure water throughout the retraction stage, although it tends to the same final equilibrium value for long observation times. This means that in order to initiate and maintain the receding movement of the contact line in drops of the polymer solution, the horizontal component of the driving force must be larger than in the case of drops of pure solvent, which suggests the existence of some sort of dissipative force arising on the contact line.

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Figure 7. Apparent dynamic contact angle for drops of pure water and PEO solution drops during the retraction stage.

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