

Dynamics of Non-Newtonian Droplets

Denis Bartolo,¹ Arezki Boudaoud,² Grégoire Narcy,² and Daniel Bonn^{2,3,*}

¹*Physique et Mécanique des Milieux Hétérogènes, PMMH, ESPCI, Paris 6, Paris 7, UMR CNRS 7636, 75231 Paris cedex 5, France*

²*Laboratoire de Physique Statistique, Ecole Normale Supérieure, 75231 Paris Cedex 05, France*

³*Van der Waals-Zeeman Institute, University of Amsterdam, 1018XE Amsterdam, The Netherlands*

(Received 22 March 2007; published 26 October 2007)

We study the impact and subsequent retraction dynamics of aqueous liquid droplets upon high-speed impact on hydrophobic surfaces. Often a spectacular “rebound” of the droplet can be observed: after the impact and expansion, the drop retracts rapidly, leading to ejection of part of the material from the surface. We show how non-Newtonian flow properties can be used to slow down the retraction sufficiently to completely inhibit rebound. The slowing down is due to non-Newtonian normal stresses generated near the moving contact line of the droplet. We provide a quantitative theory for the slowing down, and show that the non-Newtonian effects profoundly change the contact line dynamics.

DOI: [10.1103/PhysRevLett.99.174502](https://doi.org/10.1103/PhysRevLett.99.174502)

PACS numbers: 47.55.dr, 68.08.-p, 83.80.Rs

Control of droplet deposition is of paramount importance in a wide range of industrial processes, e.g., inkjet printing [1], pesticide deposition [2], and spray painting [3]. For all these applications, one wants to efficiently deposit liquids on solid surfaces. Two phenomena strongly limit the efficiency of spray deposition on nonwetting solid surfaces: splashing and bouncing [4]. Bouncing is the limiting factor for deposition of small and, or, low speed droplets. This is the major problem for instance for the deposition of aqueous pesticides on hydrophobic plant leaves, where rebound can lower the efficiency of spray deposition up to a factor of 2 [2]. Different solutions exist to improve deposition and inhibit rebound. Surfactant additives that change the wetting properties are commonly used in applications [5] but often change the drop size distribution of the spray in an undesirable manner. As an alternative, polymer additives have been suggested to prevent droplet bouncing by intervening in the fluid rheology. Adding minute quantities of polymers can dramatically slow down the retraction of aqueous drops on hydrophobic surfaces. However, despite considerable effort, so far the physical mechanism at work has remained both elusive and controversial [6–8]. In this Letter we solve the apparent contradictions that emerge from the previous experiments, and provide a quantitative explanation for the slowing down of the contact line by polymers.

From a fundamental point of view, understanding droplet motion on solid surfaces is a challenging task even for Newtonian fluids. The difficulty arises from the ubiquitous singularity of the viscous stress at the contact line, see, e.g., [9,10] for recent advances. Non-Newtonian flow properties may alter the singularity in nontrivial ways, and so shed some light onto the moving contact line problem. However, very little is known about the effect of non-Newtonian properties on the contact line dynamics. For polymer solutions, the non-Newtonian effects can be either shear thinning (an effective viscosity that decreases with increasing flow rate), or elastic effects. For the spreading of droplets, theory suggests that shear thinning effects can

remove the hydrodynamic singularity at the contact line. Experiments on the other hand show that the effects of both shear thinning and elastic effects on the spreading dynamics are small [11,12]. Conversely, we show here that for the dewetting of surfaces following drop impact, the contact line dynamics is profoundly changed. We uncover the detailed mechanism of the action of the polymers and demonstrate that the slowing down can be attributed to *nonlinear* elastic effects near the moving contact line. We find that the polymers generate strong normal stresses [13], which can be measured in conventional rheology and can be used to quantitatively account for the strong slowing down of the retraction. More precisely, we show that the contact line dynamics is ruled by the competition between the surface tension that drives the retraction and the elastic normal stresses that counter it. An important consequence of this competition is the *linear* dependence of the speed on the small-scale cutoff that allows the contact line to move despite the no-slip boundary condition. In our case the strong (linear) dependence opens the way to quantifying this microscopic length scale, which is a much debated issue for Newtonian fluids where the dependence on the cutoff is only logarithmic [14].

We study the impact and subsequent retraction of aqueous drops onto a hydrophobic surface. Three different long and flexible polymers have been used: polyacrylamide (PAM), molecular weight $M_w = 15 \times 10^6$ amu, and polyethylene oxide (PEO) of molecular weight $M_w = 4 \times 10^6$ and $M_w = 8 \times 10^6$ amu. The surface tension of the solution measured with the pendant drop method does not show a significant dependence on the polymer concentrations; $\sigma = 66 \pm 3$ mN/m for both polymers, very close to the surface tension of pure water [15,16]. The surface we used is parafilm, which is hydrophobic. For other nonwetting surfaces such as plexiglass and polycarbonate, qualitatively similar results were obtained. The receding contact angle for water on parafilm is $\theta_R \sim 90^\circ$. In addition, the surface has a low contact angle hysteresis and allows us to obtain highly reproducible results. The drops are made

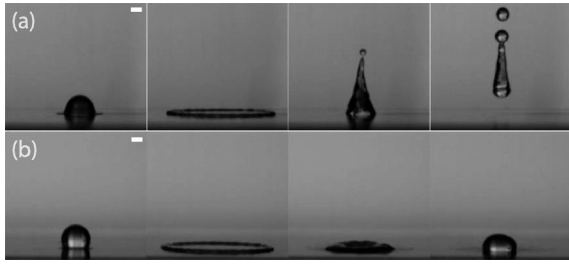


FIG. 1. Typical photographic sequence (left to right) of two aqueous drops impacting a parafilm film. Drop diameter: $D = 2.4$ mm, impact velocity: $2.5 \text{ m} \cdot \text{s}^{-1}$. Images taken at 2000 frames/s. (a) Water droplet. (b) dilute aqueous solution of polyacrylamide molecular (PAM) weight $M_w = 15 \times 10^6$ amu, concentration 500 ppm.

using a precision needle which enables a controlled release of spherical drops of radius $D = 2.5 \pm 0.2$ mm. The impact velocity of the droplets is varied simply by increasing the fall height. We have restrained our experiments to fast impacts characterized by impact Weber numbers $We = \rho D V_{\text{impact}}^2 / \sigma$, comprised between 50 and 200. We used a fast camera (1000 frames/s) to analyze the impact events.

The experimental observations are the following. Droplets impacting with high speed on a solid nonwetting surface expand upon impact, but subsequently retract rapidly. If the retraction is sufficiently violent, the droplet bounces off the surface [17]. During the impact and expansion stages, the kinetic energy of the droplet is partly transformed into surface energy and the droplet spreads out in a “pancake” form [18]. Subsequently, to relax its surface energy, the droplet retracts violently, leading to the formation of a liquid column that detaches from the surface: we observe droplet rebound. The droplets rebound if the retraction velocity exceeds a critical value [6,19]. Comparing typical snapshots for pure water, Fig. 1(a), and a dilute solution of long flexible polymers (0.5 g/l Polyacrylamide), Fig. 1(b), shows that the polymers slow down the retraction so much that the entire droplet remains stuck to the surface: rebound is completely suppressed. For a more quantitative picture, from the high-speed images, we follow the contact radius $R(t)$ in time. The important observation is that both with and without polymers, the drops expand to almost the same diameter; see Fig. 2. This is due to the fact that we study drops with low shear viscosities (at most $20 \text{ mPa} \cdot \text{s}$) and high impact Weber number ($We > 100$), leading to inertially dominated impact and expansion stages for both experiments [18,20]. Figure 2 also shows that a well-defined retraction velocity V_{RET} can be extracted from each experiment. Increasing polymer concentration decreases the retraction velocity. For the high molecular weight PEO solution, a slowing down with a factor of 25 with respect to pure water is achieved.

We verified that adsorption of the polymers onto the surface (modifying the hydrophobicity of the surface) is not at the origin of the slowing down of the fluid retraction.

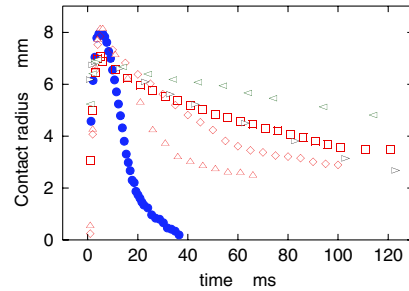


FIG. 2 (color online). Temporal evolution of the contact radius of droplets. Circles: pure water droplets. Triangles, diamonds, and squares: aqueous solution of PAM (respectively 0.5, 1 and 2 g/l). Left triangle: aqueous solution of PEO, $M_w = 8 \times 10^6$ amu (0.5 g/l). Right triangle: aqueous solution of PEO, $M_w = 4 \times 10^6$ amu (0.5 g/l). For each drop, the retraction velocity V_{RET} is determined by making a linear approximation of the initial straight line portion of the data. Droplet radius is 1.3 mm, impact speed is $2.5 \text{ m} \cdot \text{s}^{-1}$.

This was concluded, first, from the observation that both the advancing and receding contact angles of polymer solutions and of pure water only differ by a few degrees. Second, experiments with surfaces that had been dipped into the polymer solutions and dried afterwards showed results identical to those obtained on “fresh” surfaces both for water and polymer solutions. Finally, we used two chemically different polymers (PEO and PAM), and found a correlation of the slowing down of the retraction only with the bulk rheology. The shear viscosity of these polymer solutions, Fig. 3(a), remains relatively close to the viscosity of water. Previous results for Newtonian liquids show that for our experimental parameters the shear viscosity has negligible influence on the retraction speed. The same experiment carried out with water-glycerol mixtures having the same Newtonian viscosity as the polymer solutions leads to retraction speeds that are an order of magnitude higher [21]. Consequently, the viscosity increase due to the polymer addition cannot account for the strong decrease in the retraction velocity.

The large resistance to stretching or non-Newtonian elongational viscosity η_e of such dilute polymer solutions has been invoked to explain the slowing down of the droplet retraction. In [6,8], a clear correlation between the retraction speed and the elongational viscosity was reported. However, this cannot be the correct explanation for two reasons. First, η_e depends on the total deformation of the droplet, and thus should act in a similar way for the retraction and for the expansion. Besides, the global extension rate is much larger during the expansion stage. Hence, if elongational viscosity were at work to slow down the fluid retraction, it would also strongly reduce the maximum radius. Conversely, we observe in the experiments that the polymer-laden droplets expand to the same or a very similar maximum radius. Second, the impact of droplets on small cylindrical targets shows no dramatic slowing down of the retraction of the water sheet formed

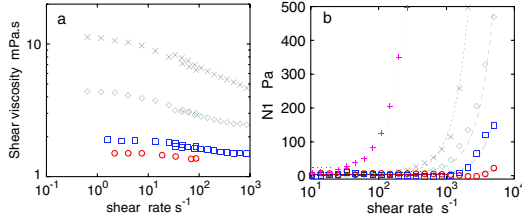


FIG. 3 (color online). Rheology of the PAM polymer solutions, molecular weight $M_w = 15 \times 10^6$ amu. Shown are: (a) The viscosity (concentrations: 0.2, 0.5, 1, and 2 g/l). (b) The first normal stress difference for different polymer concentrations (concentrations: 0.2, 0.5, 1, 2 and 5 g/l). The lines are fits with a quadratic function as discussed in the text. A Reologica Stress-Tech rheometer equipped with a cone-plate geometry was used to measure the first normal stress difference. The cone is 55 mm in diameter and has an angle of 0.5° , thus allowing for measurements of extremely small normal forces at very high shear rates. A Contraves low shear rheometer was also used for the viscosity measurements.

after impact upon addition of polymers [7]. This situation is much closer to a purely elongational flow than the impact on a solid surface, and thus should lead to a strong slowing down, again in contradiction to experiments. Therefore, the ensemble of these observations poses a serious problem.

We find that the key to solve these apparent contradictions lies in the non-Newtonian normal stress effects exhibited by these polymer solutions. If a solution of sufficiently flexible polymers is subjected to a velocity gradient normal to the flow direction, a difference in stress, N_1 , between the flow direction and the direction perpendicular to it develops due to the stretching of the polymer chains. Normal stresses, N_1 , and the shear rate, $\dot{\gamma}$, are related by a simple quadratic constitutive equation: $N_1 = \Psi_1 \dot{\gamma}^2$ (for not too large shear rate) [13]. In this case the first normal stress coefficient Ψ_1 characterizes the fluid. N_1 can be measured on a standard rheometer equipped with a normal force transducer, Fig. 3(b), or deduced from the polymer viscosity by invoking a microscopic model for the behavior of the polymer chains under flow [22]. To estimate the importance of this normal stress, it must be compared to the viscous stress. The ratio of the two stresses is: $(\psi_1/\eta)\dot{\gamma}$, which defines a characteristic time scale $\tau \equiv \psi_1/\eta$ that is directly related to the relaxation time of the polymer chains. First, during the retraction stage, an upper bound $\dot{\gamma}$ can be approximated by (V_{RET}/h) with h the height of the pancake droplet at the onset of retraction. Second, τ can be inferred directly from the rheological measurements, Fig. 3. We have chosen polymer chain lengths and concentrations such that the normal stresses are much larger than the viscous ones; in all our experiments the relaxation time exceeds $1/\dot{\gamma}$ by at least 1 order of magnitude [23].

We show now that normal stresses can be used to quantitatively predict the drop retraction velocity, and solve the apparent contradiction that emerged from the previous

measurements. To do so, we propose a simple model to describe motion of the contact line, relating its velocity V to the large scale dynamic contact angle θ . An equation that generalizes the lubrication equation for thin films was derived in [12], accounting for normal stresses in addition to shear stresses and capillarity. In the limit $\psi_1/\eta\dot{\gamma} \gg 1$, this equation relates the height profile of the drop surface $h(x, t)$ and $v(x, z, t)$, the velocity field in the drop:

$$\psi_1(\partial_z v)^2 = -\sigma(\partial_{xx} h - \kappa), \quad (1)$$

where x is the horizontal distance away from the contact line, z the vertical coordinate, and κ the large scale curvature of the liquid wedge. Equation (1) simply describes the balance between normal stresses and surface tension. With the no-slip condition at the substrate, the resulting (stationary) velocity field is $v(z) = z(\sigma/\psi_1)^{1/2}(\partial_{xx} h - \kappa)^{1/2}$. The contact line velocity V being equal to the average of v over the drop height, it is related to the shape of the drop via:

$$\frac{8\psi_1 V^2}{\sigma h} = h^2 - 2\kappa h + c. \quad (2)$$

In order to match a large scale wedge with a slope θ , we choose the constant of integration $c = -\theta^2$ and set the large scale curvature of the wedge, κ , to 0. As the solutions to (2) have a divergent slope at the contact line ($h = 0$), we introduce the equilibrium contact angle θ_{eq} by setting $h' = \theta_{\text{eq}}$ when a microscopic thickness $h = \ell_m$ is reached. So, we infer an equation of motion: $8\psi_1 V^2/\sigma\ell = \theta_{\text{eq}}^2 - \theta^2$ which can be generalized to large contact angles in the form

$$\sigma(\cos\theta - \cos\theta_{\text{eq}}) = \frac{4\psi_1 V^2}{\ell_m}. \quad (3)$$

This equation is the balance between the driving capillary force and the dissipation by normal stresses in the wedge. Figure 4 shows that for small θ , which corresponds to the experimental situation, this equation of motion provides an excellent fit to the measured retraction velocity which turns out to be independent of the impact kinetic energy. In addition, the microscopic lengths extracted from the fit of the (V_{RET}, ψ_1) curves for each polymers are close to the lengths of the (fully extended) polymer chains [24]. Thus, for the non-Newtonian case the small-scale cutoff can be evaluated explicitly, but has a different microscopic origin than for Newtonian liquids; for these the cutoff is usually thought to be related to the van der Waals forces.

Beyond the quantitative description of the forces that dictate the retraction velocity, this simple picture also provides an explanation for the previous and apparently contradictory observations. First, the correlation of the slowing down of the retraction with an elevated elongational viscosity is clear. η_e , and the normal stress have the same origin, namely, the stretching of the polymer chains. More explicitly, simple (Oldroyd-B) or more elaborate models (e.g., FENE) of flexible polymer rheology predict that η_e is an increasing function of ψ_1 [13]. Explicitly,

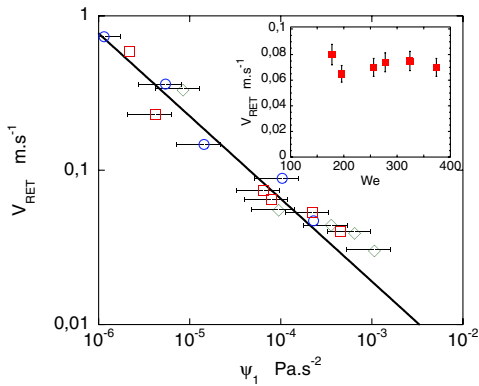


FIG. 4 (color online). Retraction velocity vs first normal stress coefficient for the three different polymers: (squares) PEO $M_w = 4 \times 10^6$ amu, (diamond) PEO $M_w = 8 \times 10^6$ amu and (circles) PAM $M_w = 15 \times 10^6$ amu, for concentrations varying from 0.200 g/l to 2 g/l. Solid line: $y = x^{-1/2}$ power law predicted by our model, Eq. (3)). Inset: Retraction velocity vs impact Weber number for a 0.5 g/l PEO solution, $M_w = 4 \times 10^6$ amu. In agreement with Eq. (3), the retraction velocity does not depend on the impact speed.

whatever the microscopic model, $\eta_e \sim \psi_1/\tau$ in the limit of small strain rates. The correlation for the retraction speed is therefore expected. Second, the absence of a polymer effect on the retraction speed after impact on a small target is also explained: in this case there is almost no shear in the liquid lamella; thus, no normal stress effect should be present to slow down the retraction dynamics, in line with the experimental observations. Finally, our arguments also explain why there is a strong effect of the polymer additive during the retraction, but not during the expansion (the maximum spreading diameter is unaffected by the polymers). This is due to the difference between the dynamic advancing and receding contact angles: the latter is much smaller than 90° , leading to a high shear rate near the contact line, where strong normal stresses are generated. On the contrary, during the expansion the same angle is close to the maximal 180° value. Hence the shear rate is much smaller, and so is consequently the normal stress which cannot hinder the liquid expansion.

In conclusion, we have shown and explained how the addition of minute quantities of flexible polymer additives can totally prevent the bouncing of liquid droplets. We have demonstrated that the important non-Newtonian effects brought about by the polymers are high normal stresses. These normal stresses counter the capillary force that drives the contact line motion, and in turn prevents rebound of the drops. We emphasize that the alteration of the contact line dynamics is not limited to the rather dilute polymer solutions considered here, but can be important for a wide variety of systems such as wormlike micelles or particle suspensions and different situations including drop impact, dewetting, and coating processes.

LPS de l'ENS is UMR8550 of the CNRS, associated with the universities Paris 6 and 7. The research has been

supported by the Foundation for Fundamental Research on Matter (FOM), which is financially supported by Netherlands Organization for Scientific Research (NWO). We would like to thank J. Meunier for helpful discussions, and G. Ducouret for help with the viscosity measurements.

*To whom all correspondence should be addressed.

bonn@lps.ens.fr

- [1] B.J. de Gans, P.C. Duineveld, and U.S. Schubert, *Adv. Mater.* **16**, 203 (2004).
- [2] W. Wirth, S. Storp, and W. Jacobsen, *Pesticide Science* **33**, 411 (1991).
- [3] S.D. Aziz and S. Chandra, *J. Energy, Heat and Mass Transfer* **43**, 2841 (2000).
- [4] R. Rioboo, C. Tropea, and M. Marengo, *Atomization and Sprays* **11**, 155 (2001).
- [5] N. Mourougou-Candoni *et al.*, *J. Colloid Interface Sci.* **192**, 129 (1997).
- [6] V. Bergeron *et al.*, *Nature (London)* **405**, 772 (2000).
- [7] A. Rozhkov, B. Prunet-Foch, and M. Vignes, *Phys. Fluids* **15**, 2006 (2003).
- [8] R. Crooks, J. Cooper-White, and D.V. Boger, *Chem. Eng. Sci.* **56**, 5575 (2001).
- [9] J.H. Snoeijer *et al.*, *Phys. Fluids* **17**, 072101 (2005).
- [10] J. Eggers, *Phys. Fluids* **17**, 082106 (2005).
- [11] S. Rafai, D. Bonn, and A. Boudaoud, *J. Fluid Mech.* **513**, 77 (2004).
- [12] A. Boudaoud, *Eur. Phys. J. E* **22**, 107 (2007).
- [13] R.B. Bird, R.C. Armstrong, and O. Hassager, in *Dynamics of Polymeric Liquids* (Wiley, New York, 1987), Vol. 1–2.
- [14] H.P. Kavehpour, B. Ovrzyn, and G.H. McKinley, *Phys. Rev. Lett.* **91**, 196104 (2003).
- [15] D. Bonn *et al.*, *Phys. Rev. Lett.* **75**, 2132 (1995).
- [16] M. Hai *et al.*, *J. Chem. Eng. Data* **43**, 1056 (1998).
- [17] A.L. Yarin *Annu. Rev. Fluid Mech.* **38**, 159 (2006).
- [18] C. Clanet *et al.*, *J. Fluid Mech.* **517**, 199 (2004).
- [19] B.P. van der Wal, Ph.D. thesis, University of Groningen, 2006.
- [20] R. Rioboo, M. Marengo, and C. Tropea, *Exp. Fluids* **33**, 112 (2002).
- [21] G. Bartolo, C. Josserand, and D. Bonn, *J. Fluid Mech.* **545**, 329 (2005).
- [22] A. Lindner, J. Vermant, and D. Bonn, *Physica (Amsterdam)* **319A**, 125 (2003).
- [23] For example, for a drop of 0.5 g/l PAM solution with an impact velocity $V_{\text{impact}} = 2.5$ m/s and an initial diameter $D = 2.3$ mm, we can estimate $1/\dot{\gamma} = V_{\text{RET}}/h \sim 10^{-4}$ s. According to the rheological measurements $\tau = 10^{-2}$ s, the normal stresses thus dominate the viscous stresses by, at least 2 orders of magnitude.
- [24] The length of the fully extended polymer chains can be estimated knowing the monomer length (PEO: 0.5 nm, PAM: 0.3 nm): PEO 72 and 36 μm , PAM 62 μm , which are of the same order of magnitude of ℓ_m deduced from the fit of the (ψ_1, V_{RET}) plots: 50 ± 10 , 33 ± 5 and 35 ± 5 μm for the PEO $M_w = 8 \times 10^6$ amu, PEO with $M_w = 4 \times 10^6$ amu and the PAM polymers, respectively.