Soft Matter

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Viscous Bouncing

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Abstract – Repellent materials are known for their ability to make impacting water recoil and takeoff, which keeps them dry after a rain. Here we show that the ability of drops to bounce can be extended by two orders of magnitude, in terms of the liquid viscosity. We measure and model two main characteristics of these viscous rebounds, namely the contact time of the drops and the elasticity of the collision, which allows us to understand how and why viscous liquids can be repelled by hydrophobic solids.

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The most spectacular property of superhydrophobic materials might be their ability to repel impinging drops [1]. Such drops successively spread (due to inertia) and recoil (due to surface tension), which eventually enables them to bounce [2]. It was argued that the expansion/retraction cycle of the drops is reminiscent of springs, where inertia and elastic force similarly conspire to generate oscillations. This analogy provides a quantitative estimate of the rebound time τ: it is expected to be the typical response time of the liquid spring, a quantity scaling as $(m/\gamma)^{1/2}$, denoting m as the mass of the drop and γ as the spring stiffness, a role endorsed here by the surface tension [3]. For water, the contact time τ is roughly 10 milliseconds for millimeter-sized drops – a time useful to estimate (and understand) when heat or chemical exchanges occur at impact: the value of τ determines the quantity of heat taken by a drop bouncing off a hot surface [4-6], or whether this drop can freeze or not when contacting a cold surface [7-9]; if additives such as surfactants are present in the liquid, comparing τ with a typical time of adsorption explains why the soapy water can still bounce despite its reduced surface tension [10-11].

Additives in water can also modify its viscosity η, and it appears useful to establish to what extent dynamic repellency can concern liquids more viscous than water. A spring recoiling in a viscous environment simply comes back to equilibrium instead of oscillating. Similarly, we anticipate that viscosity can absorb the kinetic energy at impact, as seen from a reduction of spreading when increasing η [12], leading to the suppression of the rebounds [13]. The loss of energy is quantified by the coefficient of restitution $\varepsilon = V'/V$, defined as the ratio of rebound velocity V' to the impinging velocity V. This coefficient is known for water to be a function of V: quick drops are highly deformed at impact, so that a large quantity of translational energy is transferred into vibrations, which implies a decrease of ε with increasing V [14].

Here, we discuss how viscosity affects and possibly inhibits the bouncing behavior of aqueous solutions impacting on superhydrophobic materials, which we quantify by measuring how the contact time τ and restitution coefficient ε vary as a function of the viscosity η. The solutions are water-glycerol mixtures whose viscosity is varied by more than two decades, between 1 mPa·s and 200 mPa·s, yet keeping a fairly constant surface tension $\gamma \approx 61$ mN/m. The mixture is pushed through a calibrated needle so as to control the drop radius at $R = 1$ mm. The impact velocity V can be tuned from 0.3 m/s to 1.2 m/s by playing on the height from which the liquid is released. The substrate is a flat piece of brass (with a size of a few centimeters) sprayed with

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an acetone solution of hydrophobic beads (Ultra ever Dry, Ultratech International, typical bead size of 20 nm). After solvent evaporation, the surface becomes water repellent, as evidenced by the values of the advancing and receding contact angles of water, 166 ± 4° and 159 ± 2°, respectively. Drop dynamics are recorded from the side, using a Phantom-V7 high-speed video camera shooting at 10000 frames per second.

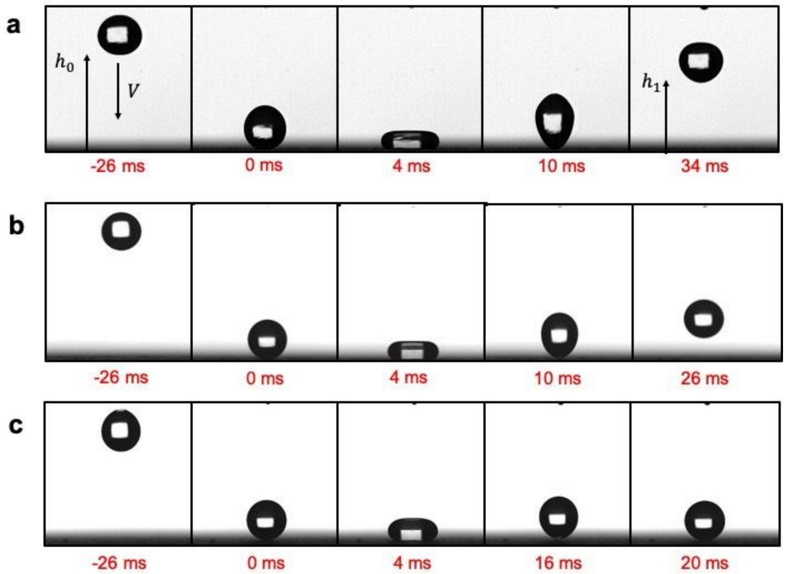

Figure 1. Bouncing sequences. Side views of drops with radius $R = 1$ mm released from a height $h_0 = 5.0$ mm and impacting on a super-hydrophobic surface with velocity $V = 0.3$ m/s. **a.** A water-drop ($\eta = 1$ mPa·s) takes off at $\tau = 10$ ms and it reaches a height $h_1 = 2.8$ mm (see also movie 1). **b.** A water-glycerol drop ($\eta = 80$ mPa·s) is able to bounce off in the same time ($\tau = 10$ ms), but the rebound is weaker ($h_1 = 0.6$ mm) (see also movie 2). **c.** A more viscous drop ($\eta = 200$ mPa·s) detaches from the surface after a significantly higher time ($\tau = 16$ ms), but it barely rises above the substrate (limit of bouncing, see also movie 3).

We compare in figure 1 the behavior of drops having similar radius ($R = 1$ mm) and impact speed ($V = 0.3$ m/s), but contrasted viscosities: $\eta = 1$ mPa·s (figure 1a); $\eta = 80$ mPa·s (figure 1b); $\eta = 200$ mPa·s (figure 1c). In figure 1a, a water drop released from a height $h_0 = 5.0 \pm 0.1$ mm impacts the solid at $t = 0$, the moment we choose for the origin of time. The drop undergoes spreading and recoils, owing to the repellent nature of the substrate, which leads to its rebound at $\tau \approx 10$ ms. Then, the drop takes off and it reaches a height $h_1 = 2.8 \pm 0.1$ mm, from which we deduce a coefficient of restitution $\varepsilon = (h_1/h_0)^{1/2} \approx 0.75$. This high value is typical of drops hitting a repellent material at a modest velocity (the Weber number $We = \rho R V^2/\gamma$ is of the order unity), a case where dissipation is minimized [14].

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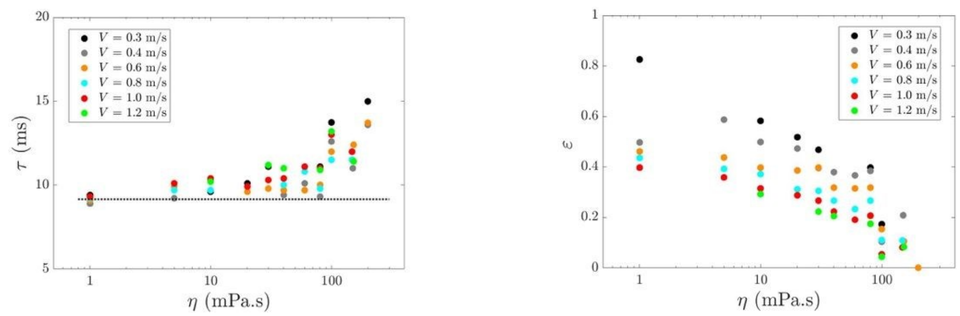
For a solution 80 times more viscous than water, we expect a much larger dissipation. However, as seen in figure 1b, the liquid keeps on bouncing. The succession of events is very close to that observed with water, the only differences being a slightly smaller maximum radius (by 15%) and a significantly lower rebound height $h_1 = 0.6 \pm 0.1$ mm, leading to $\varepsilon \approx 0.35$. Hence the increase of viscosity logically affects dissipation at impact, but not the rebound property itself – showing that repellency can be extended to highly viscous liquids. Repellency of course has a limit in viscosity, and we show in figure 1c the sequence obtained at this limit and observed for η = 200 mPa·s. On the one hand, the spreading phase still occurs in typically 4 ms, with a maximum radius smaller by 3% than in figure 1b; on the other hand, the recoiling stage now takes place in 12 ms instead of 6 ms previously, a noticeable augmentation, and the drop barely rises above the solid surface (limit of bouncing).

We plot in figure 2 how the two main characteristics of the rebound, namely the bouncing (or contact) time τ and the coefficient of restitution ε, depend on the viscosity η, at fixed drop radius (R = 1 mm) and for various impact velocities V. The supplementary information (SI) contains additional data (figures S1 and S2) that confirm our observations and conclusions.



a **b**

Figure 2. a. Contact time τ of drops with R = 1 mm as a function of the liquid viscosity η, after an impact at a velocity V on a superhydrophobic material. The dotted line underlines the contact time τ_0 for water drops. **b.** Coefficient of restitution ε (defined as the ratio of takeoff and impact velocities) as a function of viscosity η for the same set of experiments as in **a**. The standard deviation of the data is typically 5% for the contact time and less than 10% for the coefficient of restitution.

We extract from these graphs two kinds of information. 1) The bouncing time τ hardly varies with the liquid viscosity, since it increases by only 50% when multiplying η by a factor 200 (figure 2a). The scaling law established for water, $\tau_0 \sim (m/\gamma)^{1/2}$, is independent of η, since it

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results from modelling the rebound as an interplay between inertia and surface tension [3]. Even if this law (drawn with a dotted line in figure) remains close to the data at moderate viscosity (a regime where we also note the independence of τ from impact velocity V), it appears that it must be corrected to account for the slow increase of the bouncing time with η. 2) The coefficient of restitution ε of the shock is a much more sensitive marker of the effect of viscosity and impact velocity. (i) At fixed viscosity η, first, ε rapidly decreases with V, more energy being injected at large V into vibrational modes as the drop deforms more at impact [14]. In addition, the interval of values for ε has a smaller amplitude when the viscosity is larger, which is due to the smaller deformation of the drops when the liquid is more viscous. (ii) At fixed velocity V, ε decreases when increasing η, a consequence of the larger dissipation. For η = 10 mPa·s, the restitution coefficient recovers the values reported by Kolinski *et al.* for drops bouncing on flat, hydrophilic surfaces [15]. This suggests that the observed behaviors are universal, a logical result in experiments where liquids hardly (or even do not) contact their substrate so that dissipation mainly arises from internal deformations. Interestingly, the values of ε in figure 2b all remain finite (implying rebounds) below a critical viscosity η^* where ε converges to zero (transition to sticking), whatever the impact velocity. In agreement with figure 1c, η^* is observed in figure 2b to be around 200 mPa·s.

Viscous friction can damp and even inhibit the oscillations of a spring immersed in a liquid, and we wonder here whether we can extend our spring model of bouncing drops by introducing viscous damping. Friction on a repellent material is minimized, in particular because drops keep an obtuse contact angle in both spreading and receding phases. But drops strongly deform at impact for $We > 1$, so that viscous dissipation takes place inside the liquid. The scaling form of the friction force is assumed to be $(\eta V/R)R^2$, a Stokes force that we can incorporate in the spring equation: $m\ddot{r} + \eta R\dot{r} + \gamma r = 0$, where r designates a typical drop deformation and dot(s) its derivative(s) relative to time. This equation can be made dimensionless by scaling r by the drop radius R, and the time t by τ_0, which yields:

$$\ddot{x} + Oh\,\dot{x} + x = 0 \qquad (1)$$

where x is the dimensionless deformation and $Oh = \eta/(\rho\gamma R)^{1/2}$ is the Ohnesorge number, a quantity that can be seen as a Reynolds number built with the inertio-capillary velocity $(\gamma/\rho R)^{1/2}$. For millimeter-sized drops of water, we have $Oh \approx 4\text{x}10^{-3}$, a value justifying why

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viscosity could be ignored in the analysis of the rebounds of water on repellent materials. Conversely, viscous effects are expected to become dominant (and thus to prevent bouncing) when the Ohnesorge number becomes on the order of unity, which happens for a viscosity of order of 250 mPa·s, close to the threshold reported in figure 1.

We can discuss eq. (1) more carefully. Oscillating solutions (that is, bouncing) are expected provided we have $Oh < 2$, confirming the existence of a critical value of the Ohnesorge number above which dissipation suppresses repellency. In our experiments, incorporating glycerol in water slightly decreases surface tension and slightly increases the density by comparable amounts (around 15% at the maximum), so that the criterion in Ohnesorge just implies a critical viscosity $\eta^* \sim (\rho\gamma R)^{1/2}$. This result agrees with figure 2b, where the coefficient of restitution is observed to vanish when the viscosity exceeds a threshold, whatever the impact velocity. Eq. (1) can finally be solved, taking as boundary conditions $x = 0$ and $\dot{x} = V$ at $t = 0$. The classical solution of the equation is the product of a sine by an exponential, two functions that respectively reflect the bouncing behavior and the viscous damping (see the SI for details). We can deduce from this explicit solution both a contact time and a coefficient of restitution.

1) The contact time is the time τ when the spring deformation comes back to $x = 0$, which happens at $\tau \approx \pi\tau_o/(4 - Oh^2)^{1/2}$. This function diverges for $Oh = 2$, another way of manifesting the transition to sticking. At small Oh, the contact time becomes:

$$\tau \approx \tau_0 (1 + \frac{1}{8} Oh^2) \quad (2)$$

Eq. (2) expresses the increase of the pseudo-period of a damped oscillator, in agreement with the observations in figure 2a. It can be tested more quantitatively by plotting the normalized contact time τ/τ_0 as a function of Oh, as done in figure 3a. A parabolic fit drawn with dashes is found to fit the data, taking 1.0 as a prefactor of Oh^2. This value is significantly larger than the 1/8-factor in eq. (2) – but we do not expect from scaling arguments a quantitative agreement on numerical factors. The fit indicates that a numerical coefficient of order 3 in the definition of the Ohnesorge number would provide a quantitative description of the data. Note also that adding glycerol in water can favor the pinning of the liquid on its substrate, which can also contribute to a decrease of the dewetting velocity, and thus to an increase of τ.

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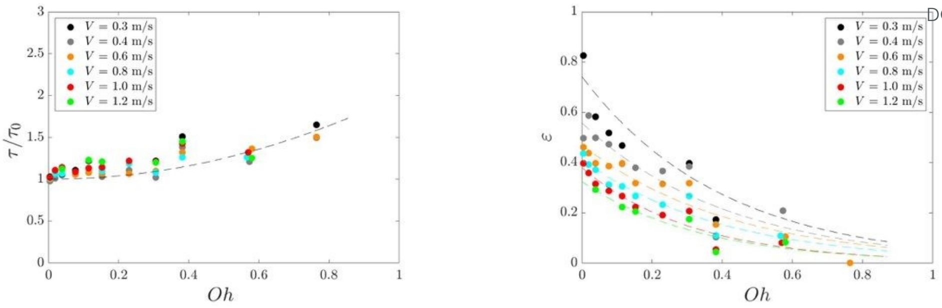

a **b**

Figure 3. a. Contact time τ of drops (R = 1 mm) with viscosity η, density ρ and surface tension γ impacting on a superhydrophobic surface at a velocity V, as a function of the Ohnesorge number $Oh = \eta/(\rho\gamma R)^{1/2}$. τ is normalized by τ_o, the contact time for water ($Oh \ll 1$), and the dotted line shows a quadratic fit with a leading order coefficient of 1.0. **b.** Coefficient of restitution ε as a function of Oh. Dotted lines represent an exponential dampening of ε for each impact velocity V, as discussed in the text.

2) We can also calculate from the solution of eq. (1) the velocity $V(\tau)$ when the spring deformation comes back to zero, which yields a coefficient of restitution $\varepsilon = V(\tau)/V$. The latter quantity can be expressed analytically, and we find $\varepsilon = \exp\,[-\,\pi Oh/(4 - Oh^2)^{1/2}]$. This exponential law predicts the existence of perfectly inelastic collisions ($\varepsilon = 0$) at finite Ohnesorge number, when the denominator in the exponential vanishes, that is, for $Oh = 2$, in agreement with the previous discussions. We saw that the fit on the contact time provides a numerical factor of ~3 in the definition of Oh, so that sticking should practically occur around $Oh \approx 0.7$, as observed experimentally. At small Oh, the law for $\varepsilon(Oh)$ becomes:

$$\varepsilon \approx \exp\,[-\,\pi Oh/2] \qquad (3)$$

We draw such exponential damping with dashes in figure 3b, after normalizing ε at $Oh = 0$ by ε_o, its velocity-dependent value. In each case, the fit with the data is convincing, in particular because the coefficient of Oh in the argument of the exponential chosen for maximizing the quality of the fit is nearly the same for all fits, that is, 2.5 ± 0.5.

Hence, despite the complexity of a phenomenon that includes a spreading phase, a maximum radius and a recoiling phase all non-trivial to describe, we found that a linearly damped spring captures the main characteristics of the rebound of viscous water. This simple model ignores the effects of the substrate, such as pinning and contact line friction, yet it allows us to understand how millimetre-size drops can be repelled up to a viscosity of ~200 mPa·s, a spectacular value since it extends dynamic repellency by two orders of magnitude in viscosity. For smaller drops, we predict that the viscous effects slowly reduce the bouncing capacity, while the rebound of larger drops is inhibited by gravity [14]. As done for the contact time τ_o at low viscosity [16], we should explore the detail of impact to derive the numerical coefficients in the formula for the contact time, when viscosity has appreciable effects. Similar detailed calculations seem more difficult for the coefficient of restitution, a quantity that implies a complete understanding of energy losses at impact – an ambitious program of research. From this point of view, our first analysis in term of scaling laws may provide a useful base for further studies.

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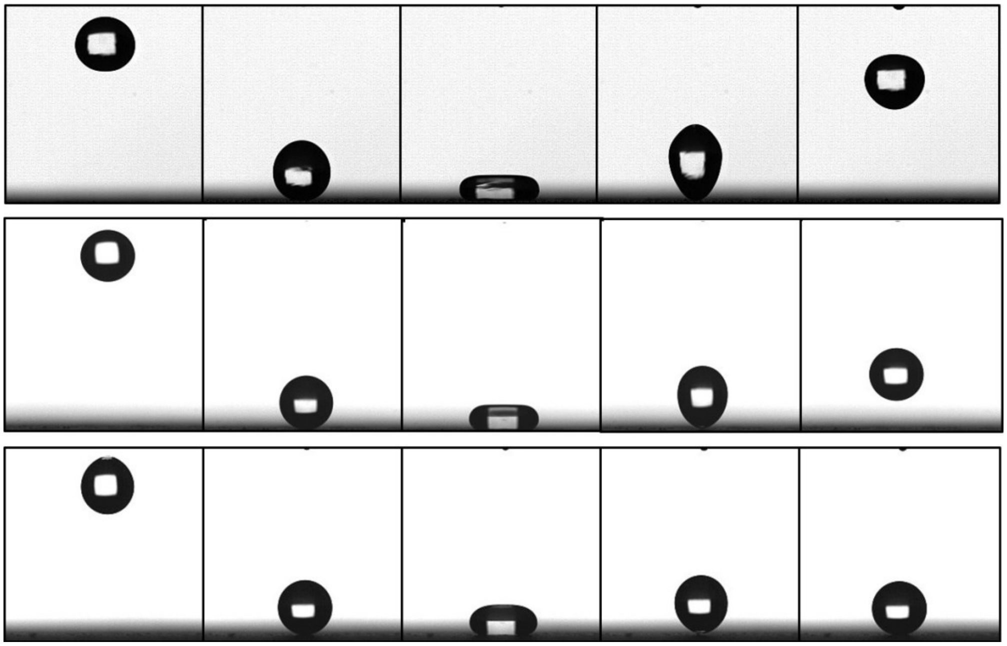

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