Measurement of Lateral Adhesion Forces at the Interface between a Liquid Drop and a Substrate

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A novel instrument allows for the first time measurements of the lateral adhesion forces at a solid-liquid interface, $f_\parallel$, in a way that is decoupled from the normal forces, $f_\perp$. We use it to measure how $f_\parallel$ between a drop and a surface is influenced by different $f_\perp$ and different histories of drop resting periods on the surface prior to sliding, t_{rest}. The variation of $f_\parallel$ with t_{rest} is similar for different $f_\perp$ and always plateaus as $t_{rest} \rightarrow \infty$. We show that the $f_\parallel$ plateau value is higher when $f_\perp$ is lower. This seemingly counterintuitive result is in agreement with recent theories.

David Tabor, who coined the term *tribology* [1], showed that the lateral force required to slide two surfaces against each other ("friction" force) is in fact proportional to the contact area. The Amonton law [2], it was then realized, is a special case in which the contact area of a rough surface happens to increase linearly with the load. In this Letter, we present a system in which the lateral force *decreases* with the normal force in spite of the fact that the contact area increases. This happens for drops on surfaces.

The problem of drops on surfaces [3] is implicated in phenomena ranging from inhalation drugs to deformable particles, self-propulsion, and ratcheting [4]. Of particular interest are the lateral forces, $f_\parallel$, associated with sliding drops on surfaces [5–9]. It has been shown that $f_\parallel$ increases with the time the drop rests on the surface prior to sliding (hereon: resting time or t_{rest}) [8,9]. This time dependent phenomenon was theoretically related [10] to the normal component of the Young equation [11], which enhances the pinning of the three phase contact line, thereby increasing the retention force [10]. Such theories, however, could not be experimentally verified due to the lack of suitable experimental instrumentation. The conventional tilt stage method [3,8,9,12,13] could not be applied for such a study due to the coupling of normal and lateral forces inherent in it. In other words, with the tilt plate the drop is never truly sessile or truly pendant, and at the extreme tilt (90°), the two converge. Additionally, the range of forces that can be applied with the tilt stage is limited between zero and the drop's weight (corresponding to 0° and 90° tilt angles, respectively). These problems were recognized decades ago [14,15] and so was a solution for both problems, namely, the use of centrifugal forces to drive the drops on the surfaces [15]. In the past, however, this solution suffered from poor monitoring of the drop *in situ* as the rotation is taking place, rendering the use of such devices impractical.

With the advancement of wireless electronics, however, we were able to construct a device in which a camera rotates *in situ* with the drop and sends the video signal in real time to a stationary computer nearby in the lab. The instrument, centrifugal adhesion balance (CAB) [16], can induce force of any practical interest and allows independent (decoupled) manipulation of the normal and lateral forces. A schematic of the CAB in Fig. 1 shows the centrifugal arm which can rotate perpendicular to the gravitational field using a dc motor. At one end of the arm, there is a plate on which a CCD camera is fixed together with a holder to place the substrate surface. This plate is fixed with respect to the arm during the rotation but can be fixed at any angle α (i.e., $0 \leq \alpha < 360°$) around an axis orthogonal to the centrifugal rotation, thereby allowing any combination of gravitational and centrifugal forces and hence independent manipulation of normal and lateral forces according to the equations:

$$f_\parallel = m(\omega^2 L \cos\alpha - g \sin\alpha), \tag{1}$$
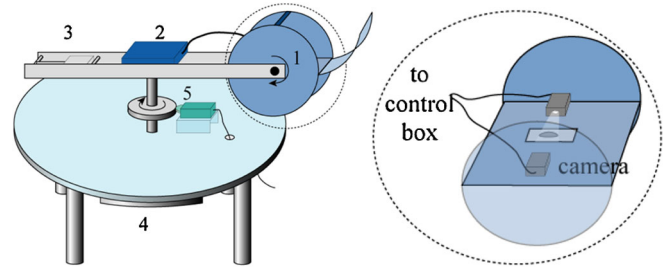

FIG. 1 (color online).   The experimental setup of the CAB. A rotating arm has a closed chamber (1) at one end and a counterbalance (3) at the other. The chamber, drawn with its door open, holds a light source and a camera between which the drop is placed as shown in the right inset. The signal from the camera is transferred to a control box (2) which runs on battery and which further transfers the signal wirelessly to a computer placed nearby outside the rotating assembly (not shown). The angular velocity is monitored using an encoder (5) that touches a round enlargement in the shaft which in turn is connected to a dc motor (4). Thus force measurements are coupled with the *in situ* video signal of the sliding object (drop in this study). By independent manipulation of the angular velocity (measured in 5) and the tilt angle (1), the CAB allows for any combination of normal and lateral forces.

$$f_\perp = m(\omega^2 L \sin\alpha + g \cos\alpha), \qquad (2)$$

where $f_\perp$ is the normal force, ω is the angular velocity, L is the distance from the center of rotation to the drop, and m is the drop's mass. Coupled to the plate is a CCD camera which records the experiment *in situ* and sends video signals in real time to a computer placed outside the rotating assembly. The drop and the camera are inside a sealed chamber at the end of the rotating arm (Fig. 1).

We start with the plate tilt values of $\alpha = 0°$ and $\alpha = 180°$ (corresponding to sessile and pendant drops, respectively). The experimental procedure is described in Fig. 2(a), while Fig. 2(b) shows corresponding pictures of a hexadecane drop on a Teflon coated silicon surface [17] inside the CAB. The traces in Fig. 2(a) describe the
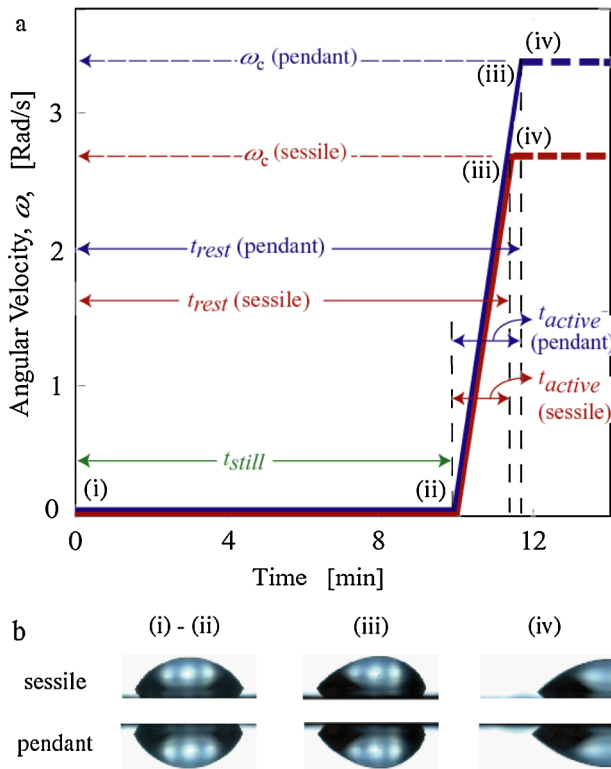

FIG. 2 (color online). The procedure of a single force datum measurement exemplified using the system of hexadecane drop on a Teflon surface [17]. (a) The variation of the angular velocity, ω, during the measurement time: the drop is allowed to rest in the stationary CAB for a prescribed period, t_{still}, after which ω is gradually increased until, at a certain critical value, ω_c, the drop starts sliding along the surface. The drop is pinned to the surface from right after placement until just before ω_c is reached; this whole time is termed t_{rest}. We consider pendant and sessile drops. (b) Drop pictures as taken at different stages of the measurement. From (i) to (ii) no lateral force is applied and the drop is symmetric and pinned to the surface; during the active stage, it is deformed as shown in (iii) but it is still pinned to the surface. Once ω_c is reached the drop slides and hence in (iv) we see only part of it in the frame. We see that the lateral force required to slide the drop is higher when the normal force is lower.

applied angular velocities, ω, as a function of experiment time. This consists of the CAB "still time," t_{still}, which is a prescribed time during which the centrifugal force is zero (the CAB remains still) followed by a CAB "active time," t_{active}, during which ω is gradually increased until, at some critical angular velocity, ω_c, the drop moves. Throughout this procedure, the drop is resting pinned to the surface and its onset of movement signifies the end of the active time, so the drop's resting time is the sum of the CAB still time and the CAB active time, i.e., $t_{rest} = t_{active} + t_{still}$. The kinetic stage following the resting time, where the drop itself moves, is a subject of other studies [12].

Two systems are reported here: one corresponds to Fig. 2 (hexadecane on Teflon) and the other, hexadecane on OTA treated mica [18], corresponds to Fig. 3, where each point is based on experiments like that shown in Fig. 2 (though for a different system). The effect of two normal forces (sessile and pendant cases) on the lateral forces required to slide the drops at various resting times is shown in Fig. 3, where the force we consider, $f_{\|c}$, corresponds to the critical angular acceleration required to slide the drop: $f_{\|c} = m\omega_c^2 L$. Figure 3 shows that the $f_{\|c}$ values increase with the resting time for both sessile and pendant drops. However, the $f_{\|c}$ values for pendant drops are higher than those for sessile. This surprising phenomenon is emphasized as the times increases further to $t_{rest} \to \infty$ when both $f_{\|c, pendant}$ and $f_{\|c, sessile}$ plateau: these plateau values are significantly higher for pendant drops compared to the same sized sessile drops. This is counterintuitive if, for example, the intuition emanates from the Amonton law or Tabor's tribological ideas [19], or even according to more specific drop-surface theories [5] where one expects the
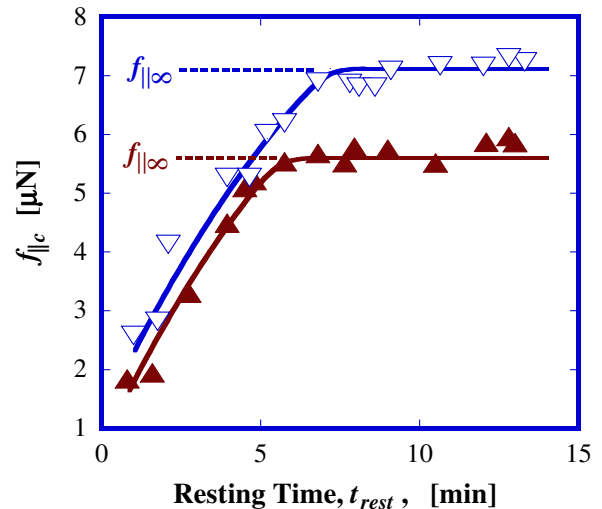

FIG. 3 (color online). The drop retention force, $f_{\|c}$, required for the onset of lateral motion of a 3.3 μl of sessile (▲) and pendant (▽) hexadecane drops on an OTA treated mica surface [23] as a function of the time, t_{rest}, that the drop rested on the surface prior to sliding. We see that the lateral force required to slide the pendant drops is higher than that for sessile drops.

three phase contact line to be the main factor retaining the drop on the surface [20].

However, theories by de Gennes and Shanahan [21] show that the unsatisfied component of the Young equation causes surface deformation, which is proportional to $\gamma \sin\theta/r$ (r is the drop's radius, γ its surface tension, and θ its contact angle with the surface). Later, Carre *et al.* proved experimentally that the deformation is indeed protruding from the surface (upwards for a sessile drop) [22]. This deformation is also associated with molecular reorientation of the solid surface [23], which strengthens the liquid-surface interaction (minimizes the free energy associated with the liquid-surface interaction) [8,9]. In line with the de Gennes–Shanahan approach, recent theories relate this stronger liquid-solid interaction to the pinning of drops to the surfaces [10] by the proportionality:

$$f_{\|c} \sim \gamma^2 \sin\theta(\cos\theta_R - \cos\theta_A), \qquad (3)$$

where the term $\gamma \sin\theta$ is related to the normal component of the Young equation, which intensifies the intermolecular reorientation with time [24], and the other prefactors (omitted here) are constant for a given surface [10]. For pendant drops, the normal component of the Young equation has a higher value (since θ is higher) and hence the molecular reorientation is more significant and the resulting intermolecular force higher. Additionally, the gravitational force in the case of pendant drops acts in the same direction as the $\gamma \sin\theta$ (pulling) and subsequently further enhances the solid molecular reorientation and resultant solid-liquid interactions while in the case of sessile drops, the two forces act in opposite directions resulting in weaker deformation and weaker subsequent liquid-solid intermolecular reorientation and hence weaker interactions and smaller retention force. Apparently, these factors overshadow the fact that the three phase contact line is longer for sessile drops compared to pendant. Experimentally, for some reason, there seems to be a good correlation just with Eq. (3), which seems to suggest that the additional influence of gravity *per se* is negligible here. For example, if we consider the angle throughout the still period (which constitutes most of the drop's rest period), we get for the sessile case $\theta_S = 33.0°$ (the index S stands for sessile). Once the system reaches ω_c, the corresponding advancing and receding angles are $\theta_{A,S} = 35.5°$ and $\theta_{R,S} = 30.3°$. For the same volume but pendant drop case, the corresponding angles are $\theta_P = 37.1°$, $\theta_{A,P} = 40.0°$, and $\theta_{R,P} = 34.7°$ (the index P stands for pendant). Putting these values in Eq. (3) once for pendant and once for sessile and dividing gives the ratio

$$\frac{\sin\theta_P(\cos\theta_{R,P} - \cos\theta_{A,P})}{\sin\theta_S(\cos\theta_{R,S} - \cos\theta_{A,S})} = 1.26,$$

which is in excellent agreement with the experimental force ratio

$$\frac{f_{\|\infty,\text{pendant}}}{f_{\|\infty,\text{sessile}}} = 1.27,$$

where $f_{\|\infty} = f_{\|c}|_{t\to\infty}$ (see Fig. 3). According to the nice agreement here and in other experiments that we conducted on this and other systems, the role of gravity to further influence the normal component and thus the intermolecular interactions seems negligible. This is in agreement with older discussions regarding the influence of gravity on Young's contact angle [11].

The agreement with theory strengthens the realization that in drops on surfaces, the case of smaller normal force, $f_\perp$, and smaller contact area results in higher lateral force required to slide the drop, $f_{\|c}$. To the best of our knowledge, this is the first experimental evidence of a smaller normal force resulting in a higher lateral force.

Figure 3 considers one drop size and one absolute value of the normal force ($f_\perp = \pm mg$). With the CAB both of these parameters can be varied. If we use different drop sizes and different normal forces, we still obtain plots that are similar to those shown in Fig. 3, though with different absolute values. Thus for a drop of 0.5μl, the ratio $f_{\|\infty,\text{pendant}}/f_{\|\infty,\text{sessile}} = 1.09$ only. The variation of the plateau value, $f_{\|\infty}$ (see Fig. 3), with the normal force, $f_\perp$, for this drop size [cf. Eqs. (1) and (2)] is shown in Fig. 4. In agreement with Fig. 3, for the same $|f_\perp|$, a greater $f_{\|\infty}$ is measured for the negative normal forces, i.e., $f_{\|\infty}(-|f_\perp|) > f_{\|\infty}(|f_\perp|)$. However, the more striking feature in this graph is that $f_{\|\infty}$ decreases as the absolute value of the normal force, $|f_\perp|$, decreases whether $f_\perp$ is positive or negative. Thus $f_\|$ increases with $f_\perp$ for positive $f_\perp$, but decreases with $f_\perp$ for negative $f_\perp$, and reaches a minimum around $f_\perp = 0$. For this drop size, very close to $f_\perp = 0$ the drop was unstable and $f_{\|\infty}$ could not be reached; however, we could verify the trend shown in the dashed line in Fig. 4
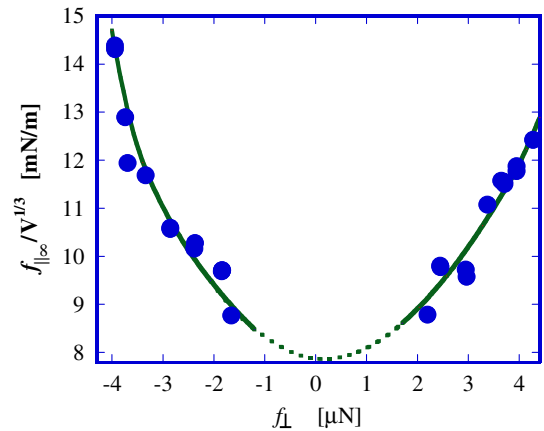

FIG. 4 (color online).   The drop retention force after reaching a time plateau, $f_{\|\infty}$ (cf. Fig. 3), required for the onset of lateral motion of a 0.5μl hexadecane drop on an OTA treated mica surface [18] versus the normal force, $f_\perp$, that the drop experiences. The lateral force is normalized by unit length (V is the drop's volume).

using smaller drop sizes (in smaller drops our current safety features do not allow the high centrifugal acceleration required for measurements far from $f_\perp = 0$).

In this experimental Letter, we do not pretend to provide a theory for this finding, and to the best of our knowledge, current theories do not address the issue in any detail to account for these novel experimental observations. The de Gennes–Shanahan approach used above for the truly pendant and truly sessile positions can explain the differences between $f_{\|\infty}$ pairs of similar $|f_\perp|$ in Fig. 4 but not the decline in $f_{\|\infty}$ as $f_\perp \to 0$. We feel, however, that the explanation should still relate to the deformation of the surface at the three phase contact line, which is apparently enhanced both by pulling normal force and by pushing normal force.

In conclusion, we introduce a novel device (CAB), using which we decoupled drop-surface lateral retention forces from their normal body forces. For a given system, orders of magnitude variation in the lateral retention force can be induced by changing the drop's normal body forces and drop's resting time. The reason for the strong influence of these two parameters on the lateral retention force is theoretically related to the normal component of the surface tension which pulls on the solid surface at the three phase contact line [21]. Topographically, this pulling [22] is insignificant in hard surfaces, but it is associated with a time dependent [8,24] molecular reorientation of the solid surface, which results in higher surface-liquid intermolecular interaction [10]. In pendant drops, the gravitational force is in the same direction as the normal component of the surface tension (pulling on the surface). Thus the total pulling force is higher, the solid surface molecular reorientation facilitated, and resultant solid-liquid intermolecular interaction and associated lateral retention force stronger than those for sessile drops in which the normal component of the surface tension and normal gravitational forces are in opposite directions. If, however, instead of just sessile and pendant drops, we induce gradual continuous variation of the normal force, we see that the change of the lateral retention force with the normal force is not monotonous, but reaches a minimum close to zero normal force (Fig. 4). This suggests that the solid surface molecular reorientation is facilitated both by pulling and by pushing body forces.

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