Study of adhesivity of surfaces using rotational optical tweezers

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Abstract
Optical tweezers are powerful tools for high resolution study of surface properties. Such experiments are traditionally performed by studying the active or the Brownian fluctuation of trapped particles in the X, Y and Z directions. Here we find that employing the fourth dimension, rotation, allows for sensitive and fast probing of the surface, and happen when birefringent microparticles are applied with circularly polarized light, thus called the rotational optical tweezers. When the trapped birefringent microparticle is far away from the surface, the rotation rate is dependent only on the laser power. However, we find that if one traps close to a surface, the rotation rate goes to zero even at finite tweezers laser powers for some specific type of substrates. We suspect this to be due to the interaction between the substrate and the birefringent particle, keeping in mind that the Faxen correction for this mode of rotation cannot increase beyond 1.2 times. We use this to probe some surfaces and find that there is no binding for hydrophobic ones but hydrophilic ones particularly tend to show a laser power threshold to start rotating. We calculate that the threshold energy of the tweezers is consistent with the Van der Waals potential energy, when the mode of interaction with the surface is purely physical. We also find that for chitosan, the mode of interaction is possibly different from Van der Waals. Further, we place the particle on the threshold and observe ‘stick–slip’ kind of rotational behaviour.

Keywords: rotational optical tweezers, adhesivity, rotation threshold

The study of adhesivity at the microscopic scales has generally been performed using atomic force microscopes (AFM) [1] by pulling a particle or tip away from a surface or dragging the tip across the surface and finding out when the bonds rupture. AFM applies a nanonewton force and can also detect interactions to a minimum of about 100 pN nm limited by the cantilever size [2]. Further, hard probing of live biological cells using AFM probes can rupture the membrane thereby killing them. Here we present an alternative technique using birefringent probes trapped in optical tweezers [3] which can probe softly [4] and sense interactions at higher resolution using the rotational degree of freedom inducing shear forces to break bonds. We turn the particle continuously using rotational optical tweezers in the proximity to the surface and find out the maximum torque at which the adhesive forces cease rotation completely. Since we do not apply a large normal force on the surface, there is no possibility of rupturing membranes of live cells either. This technique presents a new way of probing bond strengths with a shear force.

Rotational motion of a birefringent microsphere using an circularly polarized optical tweezers apparatus has been described with the following equation (1) [3]

\[ \gamma \frac{d\phi}{dt} = \tau = \eta I, \]

where, \( \gamma \) is the drag coefficient, \( \tau \) the rotational torque due to circularly polarized light, \( \eta \) the efficiency of torque transfer and \( I \) is the intensity of the tweezers light. Here, we have assumed that the gaussian varying random noise due to Brownian motion is negligible compared to the rotational torque.

We can generally conclude that the rotational rate would go to zero only when the laser intensity would be brought to...
zero. An interesting case appears when we bring this rotating microsphere close to a surface. The rotational Faxen correction to the drag is bounded to a value \((\zeta(3)\) which is about 1.20, where \(\zeta\) indicates the Riemann zeta function) very close to the surface [5, 6], thereby indicating that the rotation rate even in proximity to a surface can never become zero at a finite value of torque unless there are some other forces on the system. We perform our measurements close to some mildly hydrophilic surfaces using birefringent liquid crystalline RM257 microspheres [7] and find that the particle does stop rotating even at a finite value of torque close to a surface. We suspect that this is an effect of adhesion, which must be overcome for rotation to happen. A similar study was carried out for the translational mode of motion of a particle moving parallel to a surface when the rheology of sticking transition was studied [8]. However, this mode of translation faces much larger Faxen corrections than the yaw rotational one [9], not to mention the time scales of interaction inviting slower effects.

In order to perform the measurement, we optically trap and rotate a birefringent microparticle (liquid crystalline colloid of RM257 material (Merck), chemical name 2-methyl-1,4-phenylene bis(4-(3-(allyloxy)propoxy)benzoate) [7, 10], of diameter \(1 \pm 0.2 \mu m\), typical birefringence of 0.01) close to the top surface in an inverted microscopy configuration using the Optical Tweezers Kit (Thorlabs USA) as shown in figure 1. Colloids of RM257 are stable in water. The illumination objective is 1.25 NA, E Plan 100× oil-immersion objective from Nikon at the bottom with the illumination aperture being overfilled. The collection objective is E Plan 10×, 0.25 NA air-immersion one, also from Nikon. The laser used for optical trapping is 976 nm Butterfly laser (Thorlabs, USA). The particles are trapped close to the top surface of the sample chamber and all the measurements performed in this configuration. First, we remove the polarizer before the photodiode in the forward scatter direction and collect all the light incident to move the particle close to the surface. The scatter intensity keeps on reducing till it reaches a minimum, whereafter it keeps increasing. The extremum point of forward scattered light is attained when the particle is at the surface [5, 6], thereby indicating that the rotation rate even in proximity to a surface can never become zero at a finite value of torque unless there are some other forces on the system. We perform our measurements close to some mildly hydrophilic surfaces using birefringent liquid crystalline RM257 microspheres [7] and find that the particle does stop rotating even at a finite value of torque close to a surface. We suspect that this is an effect of adhesion, which must be overcome for rotation to happen. A similar study was carried out for the translational mode of motion of a particle moving parallel to a surface when the rheology of sticking transition was studied [8]. However, this mode of translation faces much larger Faxen corrections than the yaw rotational one [9], not to mention the time scales of interaction inviting slower effects.

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In order to estimate the rotational rate, we place a polarizer in front of the forward scatter photodiode, such that the rotational signals appear as dips in a flat background [7]. We then move on to trap the particle close to the glass surface and gradually reduce the laser power when we find a threshold beyond which the particle stops rotating. It has been shown in figure 2. At very low trapping laser powers on a glass substrate, the particle ceases to rotate. We show a couple of such data points. There is however no such threshold if a PDMS substrate is used. We explain this by considering that PDMS is hydrophobic in nature while the glass surface that we have used is hydrophilic. Then we put droplets of water onto the glass slide and estimate the contact angle which we find to be about 45°. We also consider a quartz slide that shows a contact angle of 75°, indicating that it is less hydrophilic. The respective rotation rate as a function of laser power has been shown on figure 2. In all these measurements typically on hydrophobic surfaces, we reduce the power till the rotation rate is about 1 Hz under which the trapping becomes so weak that the vertical excursions from equilibrium are comparable to the rotation events what we are trying to detect. Thus reducing laser power under such values do not
give trustworthy results, because of very weak confinement of the particle. Using a second detection laser will not make any difference because the particle would be exhibiting a lot of Brownian motion having considerable excursions from equilibrium which then become comparable to the rotational signal. However, a couple of points with no rotation have been shown in the data for the glass surface indicating that the particle indeed stopped rotating at a finite laser power. These data points could be detected because the particle stops rotation due to adhesion which is not the same in the case for PDMS. The suspensions of RM257 form stable colloids in water while the individual particle tends to stick to the hydrophilic substrates indicating that this particle itself is hydrophilic in nature.

The hydrophobic surface hardly has a threshold, as the fitted straight line passes through the origin within the error bar of the fit. However, there are noticable thresholds for the quartz and the regular glass slides, with the quartz having a lower threshold than the glass slide. It also appears that the rotation rates at higher laser powers seem to have memory of the surface. The fitted straight lines pass through a unique threshold for every surface. The experiment for the rotation rate as a function of laser power was repeated on a different day with a different Nikon 100× microscope objective at a numerical aperture (NA) of 1.3 for a glass surface, as shown in figure 3. The slope of the curve is found to be different but the threshold power remains the same at 3.9 ± 1.5 mW.

This can be explained by the following equation

\[ \gamma \frac{d\theta}{dr} = \eta (I - I_0), \]

where, \( I_0 \) is the threshold that needs to be overcome to initiate rotation. This can be understood as bonds being formed between the probe and the surface, which requires \( \eta I_0 \) amount of torque to be overcome. The slope of line is \( \frac{\eta}{r} \), which for similar types of particles would be same since \( \eta \) only depends upon the particle size and birefringence of the particle, while the \( \gamma \) depends upon the viscosity of the medium and the size of the particle. We do indeed find the slopes to be same for the three different surfaces since the sizes of all of them are about 1 \( \mu \)m. The Brenner series for Faxen corrections [5] in the presence of a hard wall bearing no-slip boundary conditions automatically takes into account the change in the viscosity of the medium close to the surface. The Brenner series of course does not include interactions between the particle and the wall and, as mentioned, the Faxen correction is bound to a value 1.20 times the away from surface value. Thus, we can only see a small reduction in the rotation rate but, unless one invokes interaction between surfaces, the complete cessation of rotational motion cannot be explained.

Further, the Faxen correction for a particle placed exactly on the surface being 1.20, and that for a 1 \( \mu \)m diameter particle placed at a separation of 100 nm between the surfaces being \( 1 - \frac{1}{2\pi r} \) which is 1.07, the error in the estimation of Faxen correction is 13%. The error bar in the estimation of the rotation threshold on glass surface is much higher than 13% - for glass surface, the error is 28%, and hence the error in estimation of the rotation frequency due to 100 nm error in estimation of separation can be neglected.

We compute the corresponding threshold energy that these particles must overcome to initiate rotation. The threshold power for rotation on glass is about 4.25 mW and the corresponding threshold \( a = -2.12 \) Hz. The drag coefficient \( \gamma = 8 \pi \eta_1 r^2 \), where \( \eta_1 \) is the viscosity of water and \( r \) is the radius of the particle. Then the coefficient \( \eta/\gamma = 0.52 \times (2\pi) \text{Hz mW}^{-1} \), such that the value of \( \eta = 8.05 \times 10^{-21} \text{pN nm Hz mW}^{-1} \).
Then, the threshold torque is \( \tau \times I_0 \) which is 34.2 pN nm and the subsequent energy is to rotate it by 360° which is 34.2 pN nm \( \times 2\pi = 215 \) pN nm. We find them to be of the order of 50–220 pN nm, as shown in figure 4. These have been plotted as a function of contact angle of a water droplet on the surface and exhibit a straight line fit within error bars. The threshold energy corresponds very well to the Van der Waals interaction [12] with a Hamaker constant of about \( 2 \times 10^{-21} \) J m separated from the particle to the surface by less than 100 nm. Thus, the rotation threshold is a good measure of the hydrophilicity of the substrate given that the mechanism of interaction is Van der Waals interaction. It may be noted here that rotational threshold energy seems to be a better indicator than threshold torque since the system only contributes to a shear force that works against the adhesion forces and cannot be compared with the pulling force required in AFM.

We show a typical curve for rotational motion of the microsphere close to the surface in figure 5(a). At high values of laser power, the particle continues to rotate periodically. However, as the power is reduced slowly, the rotation rate also reduces till a point where the rotational events start to become random. When we study waiting time distribution for the delay between two slip events (the waiting time, given as \( \tau_w \)), we find a distribution of the form figure 5(b) which can be fitted well to a Poisson distribution. This threshold behavior can be described as a stick–slip phenomena when the particle is applied with a constant small torque in the presence of the adhesion induced washboard potential. If the thermal excursions are not large enough, the particle retains it angular orientation, which we can call ‘stick’. However, when the rotational thermal noise is of large enough amplitude, the washboard barrier is breached and then the particle rotates by one turn, which we call ‘slip’. This is different from the conventional stick–slips [13] when the force applied on the system continues to rise till the slip event happens, whereafter the load goes to minimum and increases again. Since the rotational stick–slips that we infer are dependent upon the thermal fluctuations, the waiting time distribution is Poissonian in nature.

We also study the time it takes for the rotation of the particle by 180° (or the transit time for a jump between two consecutive wells in a washboard potential, given as \( \tau_r \)) during the slip events and follows a distribution given in equation (3) [14], shown in figure 5(c), expected for a biased double well potential for a barrier height \( \Delta V \)

\[
P(\tau_r) = \frac{\omega_k \sqrt{\Delta V / k_B T}}{1 - \text{erf}(\sqrt{\Delta V / k_B T})} \exp\left(\frac{-\Delta V \coth\left(\frac{\Delta V}{k_B T}\right)}{k_B T}\right),
\]

\( \text{(3)} \)
The parameter \( \omega_k \) gives a time scale for decay from the state at the higher potential to the state at the lower potential, and acts as a fit parameter here. The room temperature is \( T \) which is about 27°C for our experiments.

A tilted washboard potential can also be referred to a biased double well potential due to rotational symmetry. We estimate that the bistable potential has a barrier \( \Delta V \) of height 0.8 \( k_B T \), quite consistent with other types of such jumps in a tilted washboard potential [10, 14–16]. The value \( \Delta V \) arises as a fit parameter to the curve mentioned in figure 5(c) using equation (3). It can be compared to the average energy of rotational motion due to equipartition theorem which would have 0.5 \( k_B T \). The fact that the barrier is slightly higher than 0.5 \( k_B T \) indicates that it does not always execute rotational motion at threshold and only does so as a random event. Further, if the barrier is too high, the thermal noise is unable to provide enough energy for rotational motion. In the work of [14], such a potential barrier was shown to have a value of 1.1 \( k_B T \), quite comparable to the value we have obtained here. We can describe such a system with an equation of the form equation (4).

Here, the combination of \( I \) and \( D \) sin(2\( \theta \)) generates the washboard. The threshold energy of 215 pN nm corresponds to the value of \( \eta I_0 \) while, the potential barrier of 0.8 \( k_B T \) indicates the barrier presented by the washboard to rotational motion

\[
\gamma \omega = \eta(I - I_0) + D \sin(2\theta).
\]  

The value of \( D \) is small, compared with \( \eta(I - I_0) \), and almost equal to \( \Delta V \), such that only close to the threshold, the second term on the right hand side attains prominence. When the intensity \( I \) is much lower than the threshold, the rotation rate becomes negative which is unphysical and hence we do not see any rotations. Further, even when the intensity \( I \) is sufficiently larger than \( I_0 \), the second term on the right hand side can be neglected and hence there is no stick–slip visible in that case either. In this case, the tilt of the washboard is too large for the sinusoidal corrugation to make any effect.

We go on to study a different type of substrate where the mechanism of interaction is not expected to be of Van der Waals type, namely that of chitosan. We find that even though the contact angle for the chitosan substrate is about 75°, the threshold energy is much larger than that of glass, at 1400 pN nm. This can be explained by the fact that chitosan is a well known bio-adhesive with stickiness extending to a pH of 7 [17] thereby having a much higher threshold of rotation. We show this figure 6(a).

We also tried to perform the rotation close to a Chinese Hamster Ovary (CHO) cell which was prepared to be adhered to a glass substrate and find a very different behavior, as shown in figure 6(b). The slope of the curve seems to be much smaller (0.09 Hz mW⁻¹ compared to about 0.51 Hz mW⁻¹ in figure 2) while the threshold seems to be absent. We can explain this by considering that the threshold \( \eta I_0 \) indicated in equation (2) is dependent on frequency as

\[
\gamma \omega = \eta I - \gamma_0 \omega.
\]

Then we get the following equation where the slope can be much lower

\[
(\gamma + \gamma_0) \omega = \eta I.
\]

Although the viscous drag coefficient depends upon the particle size, the RM257 sample diameter is monodisperse to within 1000 ± 200 nm [7], also confirmed with video imaging and does not explain the low slope. This indicates that the CHO cell surface appears like a viscous medium for the rotating particle with a viscosity that is five times larger than a particle in proximity to glass. Since the trapping light enters the sample chamber from the bottom while the CHO has been attached to the substrate at the top, the cell itself has no effect on the trapping light. This kind of effect has also been reported in a similar work using translational motion close to the surface upon the influence of specific binding to the surface [18]. We suspect that our increase in drag is due to partial nonspecific binding to the surface of the cell.
Thus, to conclude, we have demonstrated a system using birefringent microspheres which can sense the surface adhesivity. If surfaces without chemical adhesivity are used, the Van der Waals force ensures that only hydrophilic ones show rotational threshold. This can subsequently be used to determine the hydrophilicity of the surface. Further, even if other mechanisms of binding are present, the rotational threshold indicates the binding energy. We also show that at the point of threshold, particularly on the glass surfaces which are mildly hydrophilic, the rotational motion follows a stick–slip behaviour where the slip events happen randomly. This kind of technique can eventually be used to study adhesivity at the nanometric scales and is possibly a more sensitive probe than AFMs, relying on the shear force instead of the normal pulling force. We can thus ascertain the adhesional force without normal pulling on the bonds, thereby keeping the particle at the same location.

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Appendix. Materials and methods

The chitosan (Sigma-Aldrich 50000) substrate was prepared by dissolving in 5% solution of formic acid in double distilled water. We took 3% (W/V) concentration of chitosan in the formic acid solution for making the film. This solution is stirred at 75 °C for 1 h. The prepared solution is filtered and spin coated on glass substrate.

The PDMS (Dow Corning’s Sylgard 184 elastomer kit) substrate is prepared by curing the silicone elastomer in 10% (W/W) with the curing agent. The viscous solution is spin coated on glass slides and baked at 150 °C.

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References

[1] Florin E L, Moy V T and Gaub H E 1994 Science 264 415
[2] Viani M B, Schaffer T E, Chand A, Rief M, Gaub H E and Hansma P K 1999 J. Appl. Phys. 86 2258
[3] Freise M E J, Nieminen T A, Heckenberg N R and Rubinsztein-Dunlop H 1998 Nature 394 348
[4] Friedrich L and Rohrbach A 2015 Nat. Nano. 10 1064
[5] Liu Q and Prosperetti A 2010 J. Fluid Mech. 657 1
[6] Leach J, Mushifique H, Keen S, Leonardo R D, Ruocco G, Cooper J M and Padgett M J 2009 Phys. Rev. E 79 026301
[7] Ramaiya A, Roy B and Schaffer E 2017 Proc. Natl Acad. Sci. (USA) 114 10894
[8] Sharma P, Ghosh S and Bhattacharya S 2008 Nat. Phys. 4 960
[9] Roy B, Ramaiya A and Schaffer E 2018 J. Opt. 20 035603
[10] Roy B and Schaffer E 2016 Curr. Sci. 111 2005
[11] Schaffer E, Norrelykke S F and Howard J 2007 Langmuir 23 3654
[12] French R H, Winey K I, Yang M K and Qiu W 2007 Aust. J. Chem. 60 251
[13] Gao C, Kuhlmann-Wilsdorf D and Makel D D 1994 Wear 173 1
[14] Shao L, Andre D, Jones S, Johansson P and Kall M 2018 Phys. Rev. B 98 085404
[15] Pedaci F, Huang Z, van Oene M, Barland S and Dekker N H 2011 Nat. Phys. 7 259
[16] Pedaci F, Huang Z, van Oene M and Dekker N H 2012 Opt. Exp. 20 3787
[17] Mati-Baouche N, Elchinger P-H, de Baynast H, Pierre G, Delattre C and Michaud P 2014 Eur. Pol. J. 60 198
[18] Pralle A, Florin E-L, Stelzer E H K and Horber J K H 2000 Single Mol. 1 129