**INTRODUCTION**

Young’s law states that the contact angle between a liquid–air interface and an ideal solid is given by:

\[
\cos \Theta_Y = \frac{\gamma_{SL} - \gamma_{SA}}{\gamma}
\]  

(1)

where \( \Theta_Y \) is Young’s contact angle, and \( \gamma_{SA}, \gamma_{SL} \), and \( \gamma \) are the solid–air, solid–liquid, and liquid–air interfacial tensions, respectively. Since \( \gamma_{SA}, \gamma_{SL} \), and \( \gamma \) are constant material properties for an ideal solid, eq 1 predicts that the contact angle is uniquely defined. Therefore, according to Young’s law, an ideal (solid) particle should be able to rotate freely at a liquid–air interface, as long as the interface has time to reach equilibrium (Figure 1a).

However, in reality, the (static) contact angle, \( \Theta \), does not take a single value, but it lies within a finite range, between the so-called receding and advancing contact angles \( (\Theta_R \leq \Theta \leq \Theta_A) \). A liquid only begins to advance relative to a solid when \( \Theta \geq \Theta_A \), and it only begins to recede when \( \Theta \leq \Theta_R \). This effect is called contact angle hysteresis. Contact angle hysteresis is caused by inhomogeneities on the surface of the solid and by the adaption of the solid to the liquid.\(^{2-5} \) All real solids (including particles) display contact angle hysteresis. Therefore, to rotate a particle relative to a liquid–air interface, the contact angle on the side that rolls out of the liquid must be equal to \( \Theta_R \), whereas the contact angle on the side that rolls into the liquid must be equal to \( \Theta_A \) [Figure 1b].

The influence of contact angle hysteresis on the rotation of particles at an interface is still largely unexplored, despite its potential relevance in addressing practical questions such as what causes granular matter (e.g., sand grains) to flow more slowly when moist? Dry particles easily roll and slide relative to one another.\(^{6-8} \) Unlike dry particles, moist particles are connected by microscopic liquid bridges.\(^{9-12} \) Particles connected to liquid bridges cannot roll and slide easily. Several mechanisms have been identified to explain why this is so. First of all, the liquid bridges cause an increase in adhesion...
between the particles, which results in an increase in friction. Second, the bridges form an extended network, resulting in a stiff structure. A third contribution is due to viscous dissipation within the liquid bridges. However, none of these contributions considers the influence of contact angle hysteresis on the ease with which particles can roll, even though contact angle hysteresis can significantly alter rolling friction, as shown by Schade and Marshall (2011) and Marshall (2014), who considered a particle rolling on a thin liquid film.

In this paper, we derive a general analytical expression for the resistive torque experienced by a particle rotating at an interface (Figure 1b). Surface tension always acts parallel to an interface. Therefore, on both the right and left sides of the particle, the surface tension vector has a component tangential to the particle. This tangential component produces a torque that opposes the rotation. Since the torque is caused by surface tension, we will call it capillary torque. In general, the capillary torque increases with contact angle hysteresis and has a maximum of the order of $\gamma RL$, where $\gamma$ is the surface tension, $R$ is the radius of the particle, and $L$ is the diameter of the three-phase contact line around the particle. Our results demonstrate that contact angle hysteresis is an important factor that can severely restrict rotation at an interface when the magnitude of the torque causing rotation is $<\gamma RL$.

## THEORY

### General Expression for the Torque

As a model system, we consider a spherical particle at a liquid–fluid interface. In general, the second fluid can be any gas or liquid that is immiscible with the first liquid. In the following, we will refer to the second fluid as ‘air’. Our aim is to calculate the torque required to rotate the particle about the $x$-axis that goes through its center (Figure 2). When the particle rotates counterclockwise, the liquid–air interface recedes (advances) on the right (left) side of the axis of rotation. This asymmetry gives rise to a torque about the axis of rotation

$$M = \oint_{CL} \mathbf{r}_l \times \gamma \, dl$$

(2)

where $\mathbf{r}_l$ is the perpendicular vector from the rotational axis to the contact line, $\times$ denotes the vector cross product, and $dl = R \sin \phi \, d\alpha$ is the contact line length element. The contour integral is around the contact line (CL), which we assume to be circular. $\gamma$ acts at the contact line and makes an angle $\Theta(\alpha)$ with the surface of the particle, where $\Theta(\alpha)$ is the contact angle at an azimuthal angle $\alpha$. In spherical coordinates, $\gamma$ is given by

$$\gamma = \gamma \sin \Theta(\alpha) \hat{r} + \gamma \cos \Theta(\alpha) \hat{\phi}$$

(3)

where $\hat{r}$ is the radial unit vector from the center of the sphere and $\hat{\phi}$ is the polar unit vector defined from the $z$-axis. $\mathbf{r}_l$ can most easily be expressed in terms of the Cartesian unit vectors

$$\mathbf{r}_l = R \sin \phi \mathbf{a}_y + R \cos \phi \mathbf{a}_z$$

(4)

Integrating eq 2 requires knowledge of the contact angle variation around the contact line, $\Theta(\alpha)$. $\Theta(\alpha)$ is not known for a rotating particle. However, we expect it to be analogous to contact angle variation around a drop moving on a flat surface. In both cases, there is relative motion between a solid and a liquid, with a receding contact angle on one side and an advancing contact angle on the opposite side. At the front of a moving drop, the contact angle corresponds to the advancing contact angle, whereas at the rear side, it corresponds to the receding contact angle. Several models have been proposed to describe the variation of the contact angle between these two extremities. Dimitrakopoulos and Higdon used a step function. Korte and Jacobi assumed $\Theta(\alpha)$ to be linear in $\alpha$. Extrand and Kumagai assumed that $\cos \Theta(\alpha)$ is linear in $\alpha$ and ElSherbini and Jacobi demonstrated (experimentally) that both $\Theta(\alpha)$ and $\cos \Theta(\alpha)$ can be fitted by a cubic polynomial. It turns out that the different assumptions lead to similar results, except for a different prefactor.

In the appendix, we evaluate eq 2 both for a step and a cubic variation in $\cos \Theta(\alpha)$ (Figure 3a) and obtain the following expression for the magnitude of the capillary torque

$$\frac{M}{\gamma R^2} = 2k \sin \phi (\cos \Theta_R - \cos \Theta_L)$$

(5)

where $k = 1$ for the step variation and $k = 24/\pi^3 \approx 0.77$ for the cubic variation (Supporting Information). Throughout the rest of this paper, we will use $k = 24/\pi^3$ since the cubic variation allows the contact angle to vary in a realistic (smooth and continuous) way. The net capillary torque vector points along the $-x$ direction (i.e., the torque acts clockwise) and therefore opposes the rotation. The $y$ and $z$ components of the capillary torque vector are zero due to the symmetry of the contact angle about the $yz$ plane. We can also express eq 5 in terms of the average contact angle, $\Theta = (\Theta_L + \Theta_R)/2$, and the contact angle hysteresis, $\Delta \Theta = \Theta_L - \Theta_R$

$$\frac{M}{\gamma R^2} = 4k \sin \phi \sin \Theta \sin \frac{\Delta \Theta}{2}$$

(6)

Figure 3(b) shows a plot of $M/\gamma R^2$ as a function of $\phi$, using $\Theta = 60^\circ$ as an example. $M$ has a maximum at $\phi = 90^\circ$ because the length of the contact line is largest at this position. The torque

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**Figure 2.** Particle rotating at an interface. Left: schematic of the particle rotating about a horizontal axis going through its center. The contact line is marked by points A and R. Right: the particle rotating about a horizontal axis going through its center. The contact line is marked by points A and R. The blue dotted line shows the rotational axis.
tends to zero as $\phi$ tends to 0 and 180° since the length of the contact line goes to zero at these two extremities. As the contact angle hysteresis increases, the capillary torque also increases since a higher $\Delta \Theta$ causes a more asymmetric interface.

**RESULTS AND DISCUSSION**

To gain further insights into the implications of the capillary torque, we consider two special cases: (1) when the particle rotates about its static equilibrium position at an air–water interface (Figure 4a) is relevant to describe particles adsorbed at the surface of a lake, on the surface of a lake, on the surface of a lake, or on the surface of droplets in a Pickering emulsion.27,28 (b) Capillary torque acting on a sphere (average contact angle, $\Theta = (\Theta_\lambda + \Theta_\delta)/2 = 60^\circ$) as a function of polar angle, $\phi$. The capillary torque increases with contact angle hysteresis, $\Delta \Theta = \Theta_\lambda - \Theta_\delta$, as shown by the different curves.

**Figure 3.** (a) Particle rotating at an interface. The contact line is assumed to be circular (dashed red). (b) $\cos \Theta(\alpha)$ is assumed to follow a cubic polynomial in $\alpha$. (b) Capillary torque acting on a sphere (average contact angle, $\Theta = (\Theta_\lambda + \Theta_\delta)/2 = 60^\circ$) as a function of polar angle, $\phi$. The capillary torque increases with contact angle hysteresis, $\Delta \Theta = \Theta_\lambda - \Theta_\delta$, as shown by the different curves.

**Figure 4.** (a) Static particle in equilibrium at a liquid–air interface ($\phi = \Theta$). (b) Capillary torque as a function of average contact angle when the particle rotates about its initial equilibrium position.

\[
M^p = 4\gamma k R^2 \sin \Theta \frac{\Delta \Theta}{2}
\]  

(7)

$M^p$ is symmetric around $\Theta = 90^\circ$ and it increases with contact angle hysteresis (Figure 4). We have restricted our results to a maximum contact angle hysteresis of $\Delta \Theta = 50^\circ$ since our assumptions about the shape of the contact line might no longer be appropriate for very large $\Delta \Theta$.

Practically, most particles are mildly hydrophilic to mildly hydrophobic (mean contact angle is approximately between 30° and 90° with water). Special treatments, such as plasma cleaning or the addition of nanoscale roughness, are usually required to achieve lower or higher average contact angles with water. Therefore, for most practical cases, the torque required to rotate a particle about its equilibrium position at an air–water interface is of the order of $\gamma R^2$ (Figure 4b).

**Brownian Motion at an Interface.** In thermal equilibrium, small particles exhibit Brownian motion. When particles are in Brownian motion at an interface, the translational motion is constrained to the two-dimensional interface.29,30 Furthermore, as we will show below, particles at an interface do not rotate as they would do when fully dispersed in the liquid. Rotation becomes negligible since it is opposed by capillary torque.

Here, we quantify this effect by calculating the root-mean-square angle through which thermal energy rotates a particle at an interface. As an example, we consider a hydrophobic particle with $\Theta = 90^\circ$, resting in equilibrium (half-submerged) at a horizontal air–water interface. In the complete absence of external forces, $\theta = \Theta = 90^\circ$, along the entire contact line. When small rotational forces are applied, the contact line on the particle will remain pinned unless the angular rotation out of the plane of the interface is greater than half the contact angle hysteresis.

At room temperature, thermal energy will attempt to vibrate and rotate the particle. When thermal energy rotates the particle counterclockwise by a small angle $\theta$, the contact angle on the right side becomes $\Theta - \theta$, and the contact angle on the left becomes equal to $\Theta + \theta$. Therefore, by substituting $\Delta \Theta = 2\theta$ (and $\Theta = 90^\circ$) in eq 7, we obtain the magnitude of the capillary torque resisting the thermal rotation as $M = 4\gamma k R^2 \sin \theta$. 

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Since we anticipate \( \vartheta \) to be small (an assumption that we will show to be valid below), we can write \( \sin \vartheta \approx \vartheta \). The work required to overcome capillary torque and rotate the particle by \( \vartheta \) about the \( x \)-axis is

\[
W = \int_0^\vartheta M d\vartheta' = 4\gamma k R^2 \int_0^\vartheta \vartheta' d\vartheta' = 2\pi \vartheta' R^2
\]

As \( W \) is quadratic in \( \vartheta \), we can apply the equipartition theorem. According to the equipartition theorem, the thermal energy accessible to each rotational degree of freedom is \( k_B T/2 \), where \( k_B \) is the Boltzmann constant and \( T \) is the absolute temperature. Since capillary torque influences rotation about the \( x \)- and \( y \)-axes, there are two degrees of freedom for rotation against the interface. Therefore, the average potential energy associated with rotating the particle against the interface is \( \langle W \rangle = k_B T \). By equating \( \langle W \rangle \) to eq 8, we obtain the root-mean-square angular displacement caused by Brownian motion

\[
\sqrt{\langle \vartheta^2 \rangle} = \frac{1}{2} \frac{k_B T}{2\pi k R} \frac{1}{2}
\]

For a nanoparticle with a radius of 50 nm (e.g., soot) at the surface of water (\( \gamma = 72 \text{ mN m}^{-1} \) and \( T = 300 \text{ K} \)), \( \sqrt{\langle \vartheta^2 \rangle} \approx 0.2 \). For a 10 \( \mu \text{m} \) particle, the angle decreases to 0.01\(^\circ\). Since all real particles have a contact angle hysteresis much greater than these values, thermal energy is insufficient to overcome contact line pinning and cause the particles to rotate relative to the interface. Hence, thermal fluctuations will only be able to rotate nano- and microparticles by negligible amounts. Every time thermal fluctuations cause the particle to rotate, the pinned contact line will restore it back to the equilibrium configuration, thus preventing any continuous rotation.

**Particle Surrounded by a Meniscus.** When a hydrophilic particle is placed in contact with a hydrophilic surface in air, a water meniscus forms around the contact region due to the condensation of water vapor from the atmosphere (Figure 5a).\(^{1,3,5}\) Capillary condensation leads to an increase in the rotation.

**Figure 5.** (a) Particle rolling on a flat surface with a liquid meniscus between the particle and the surface. (b) Capillary torque as a function of average contact angle, \( \Theta = (\Theta_A + \Theta_R)/2 \), for different contact angle hysteresis, \( \Delta \Theta = \Theta_A - \Theta_R \).

Equation 10 is also valid for a particle rolling on a thin liquid film, like in the experiments performed by Bico et al.\(^{33}\) and Schade and Marshall (2011).\(^{16}\) However, in this case, capillary torque is only one of the several contributing factors to the resistive force acting on the particle. For a full description, the solid–solid rolling friction, which arises due to deformation losses and due to the energy required to peel the rear contact between the two solid surfaces,\(^{34}\) has to be included. Furthermore, the viscous forces and Laplace pressure distribution inside the meniscus have to be considered.\(^{17}\)

The relative importance of each of these contributions depends on the material properties (viscosity, surface roughness, viscoelastic properties, and surface energies) of the particle, the flat substrate, and the liquid meniscus.\(^{17}\)

Interestingly, capillary torque implies that the onset at which a particle begins to roll on a wet inclined surface occurs at a finite angle of inclination, even when there is no solid–solid rolling friction between the particle and the surface. To gain intuition on how significant the capillary torque is, we consider a particle on a flat surface tilted by an angle \( \alpha \) to the horizontal. Our aim is to calculate how large the particle has to be for it to begin rolling down the inclined surface. We assume that the contact lines between the meniscus and the particle and between the meniscus and the flat surface remain pinned until rolling starts. The onset of rolling occurs when the driving torque due to the particle’s weight becomes equal to the capillary torque. The torque produced by the weight of the particle is \( mgR \sin \alpha \), where \( m \) is the mass, \( g = 9.81 \text{ m s}^{-2} \) is the gravitational acceleration, and \( R \) is the radius of the particle, whereas the capillary torque is given by eq 10. Rolling only starts when

\[
M = \gamma k R (\cos \Theta_R - \cos \Theta_A)
\]

(10)
The force required to move a drop on a flat surface or rotate a particle at an interface can be conveniently estimated when there is a liquid meniscus between the particle and the surface. Therefore, an estimate for the capillary torque that a particle rotating at an interface experiences is similar to the expression for the friction force between a moving drop and a flat surface.

\[
F = γk(\cos Θ_R - \cos Θ_a)
\]

where \( L \) is the diameter of the contact line and \( k = 24/\pi^3 \) for a cubic contact angle variation. The prefactor \( k \) may vary depending on the precise contact line geometry and contact angle variation. In the case of the rotating particles, the effective force given by eq 13 corresponds to a force applied tangentially along the circumference of the particle.

We can take advantage of the similarity of the scenarios sketched in Figure 6 to indirectly determine the capillary torque (experimentally). Several methods have been developed to measure drop friction on various surfaces. In contrast, it is unusual, as well as practically challenging, to measure the torque required to rotate a small particle at an interface.

Therefore, an estimate for the capillary torque that a particle made of material B would experience when it rotates at the interface between liquid A and air can be conveniently obtained by instead measuring the force required to move a drop of liquid A on a flat surface of material B.
The \( \hat{y} \) component of the integral is

\[
M_y = \gamma R^2 \int_0^{2\pi} \sin \Theta(\alpha) \sin \phi \cos \alpha \, d\alpha \tag{20}
\]

\( M_y \) evaluates to zero because the terms in \( \alpha \) are \( \sin \Theta(\alpha) \cos \alpha \) and \( \cos \Theta(\alpha) \cos \alpha \), which both evaluate to zero when integrated from 0 to \( 2\pi \). These terms integrate to zero because \( \sin \Theta(\alpha) \) and \( \cos \Theta(\alpha) \) are even functions about the \( yz \) plane, whereas \( \cos \alpha \) is an odd function.

Hence, overall, the integrand is an odd function and therefore integrates to zero.

The \( \hat{z} \) component of the integral is

\[
M_z = -\frac{\gamma R^2}{2} \int_0^{2\pi} \sin \Theta(\alpha) \sin^2 \phi + \cos \Theta(\alpha) \cos \phi \sin \alpha \, d\alpha = 0 \tag{21}
\]

\( M_z \) evaluates to zero because the terms in \( \alpha \) are \( \sin \Theta(\alpha) \sin 2\alpha \) and \( \cos \Theta(\alpha) \sin 2\alpha \), which are both odd functions about the \( yz \) plane. Intuitively, \( M_z = 0 \) and \( M_y = 0 \) are expected due to the symmetry of the surface tension vector about the \( yz \) plane. Any surface tension component that produces a moment along the \( yz \) plane, \( \alpha \) is canceled by an equal and opposite component pointing along \( -y \) or \( -z \), respectively. Thus, the only nonzero torque component is \( M_x \). Since the capillary torque opposes rotation, we expect \( M_x \) to be negative. As we are interested in the magnitude of the torque, we will consider \( -M_x \) which is positive. In the following, we will also drop the subscript and simply refer to \( -M_x \) as \( M_x \).

For simplicity, we first consider a circular contact line divided between an advancing and a receding side with the following contact angle dependence

\[
\Theta(\alpha) = \begin{cases} 
\Theta_R & 0 < \alpha < \pi \\
\Theta_A & \pi < \alpha < 2\pi
\end{cases}
\tag{22}
\]

For this case, eq 19 (without the negative sign) can be written as

\[
\frac{M_x}{\gamma R^2} = \int_0^\pi \cos \Theta(\alpha) \sin \alpha \cos \phi \sin \alpha \, d\alpha + \int_\pi^{2\pi} \cos \Theta(\alpha) \sin \alpha \cos \phi \sin \alpha \, d\alpha = 2 \sin \phi (\cos \Theta_R - \cos \Theta_A) \tag{23}
\]

When a more realistic and complex expression is used to describe \( \Theta(\alpha) \), the resulting expression is similar to eq 23, but with a different prefactor

\[
\frac{M_x}{\gamma R^2} = 2k \sin \phi (\cos \Theta_R - \cos \Theta_A) \tag{24}
\]

When \( \cos \Theta(\alpha) \) is given by a cubic polynomial in \( \alpha \), we obtain \( k = 24/\pi^2 \) (Supporting Information).

Alternatively, we can write eq 24 as

\[
\frac{M_x}{\gamma R^2} = 4k \sin \phi \sin \Theta \sin \frac{\Delta \Theta}{2} \tag{25}
\]

where \( \Theta = (\Theta_A + \Theta_R)/2 \) is the mean contact angle and \( \Delta \Theta = \Theta_A - \Theta_R \) is the contact angle hysteresis. The following trigonometric identity was used to arrive at eq 25 from eq 24

\[
\cos A - \cos B = -2 \sin \frac{A + B}{2} \sin \frac{A - B}{2} \tag{26}
\]
