%% LyX 2.3.6 created this file. For more info, see http://www.lyx.org/.

%% Do not edit unless you really know what you are doing.

\documentclass[english]{achemso}

\usepackage[T2A,LGR,T1]{fontenc}

\usepackage{babel}

\usepackage{array}

\usepackage{textcomp}

\usepackage{url}

\usepackage{multirow}

\usepackage{amsmath}

\usepackage{graphicx}

\usepackage{subscript}

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breaklinks=false,pdfborder={0 0 0},pdfborderstyle={},backref=false,colorlinks=false]

{hyperref}

\makeatletter

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% LyX specific LaTeX commands.

\title{Wetting of adhesive fluid controls insect adhesion in air and underwater}

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\DeclareRobustCommand{\greektext}{%

\fontencoding{LGR}\selectfont\def\encodingdefault{LGR}}

\DeclareRobustCommand{\textgreek}[1]{\leavevmode{\greektext #1}}

\ProvideTextCommand{\~}{LGR}[1]{\char126#1}

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\fontencoding{T2A}\selectfont\def\encodingdefault{T2A}}

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\text{\ifx\math@version\b@ld\bfseries\fi#1}\endgroup\else#1\fi}

%% Because html converters don't know tabularnewline

\providecommand{\tabularnewline}{\\}

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% User specified LaTeX commands.

\SectionNumbersOn

%\setkeys{acs}{doi = true}

\setkeys{Gin}{width=\linewidth}

\usepackage{subcaption}

\makeatother

\begin{document}

\begin{abstract}

Insects like beetles can stick to various surfaces using hairy pads

mediated by an oily adhesive fluid.

% Is the role of the adhesive fluid so established that people would agree than they cause adhesion? My understanding was that they may contribute but not that there role is so important. The problem is that one of our main message is that they are relevant. If this is already common knowledge, we have less news.

It was previously shown that the

pads can even attach underwater, presumably due to an air bubble trapped

around the pad. However, the bubble's ~~relative~~ contribution to adhesion

via capillary force remained~~s~~ unclear. To investigate the ~~exact~~ role

of the bubble, ~~in this study,~~ we measured~~perform~~\emph{ in-vivo} underwater adhesion

~~measurements~~ of a ladybug's pad, in the presence and absence of the

trapped bubble and compare it with its adhesion in air. Our experiments

reveal that on a hydrophobic substrate, even without a bubble, the

pad can show adhesion underwater comparable to that in air. On a hydrophilic

substrate, underwater adhesion is significantly reduced, with or without

a trapped bubble. To explain these results, we develop a simple theoretical

model for~~to estimate~~ the net adhesion of a hairy pad due to capillary

forces. Our results demonstrate that the wetting properties of the

adhesive fluid determines the insect's adhesion in both air and underwater

conditions.

\end{abstract}

\section{Introduction}

The question of how insects and other small animals can walk on smooth surfaces against gravity

has fascinated scientists for at least the past three centuries \cite{RN198,RN59}.

We now know that such animals are able to adhere by using specialized

organs on their feet called adhesive pads. These adhesive pads exist

in a variety of types depending on the animal, but are generally categorized

into: 1) ``smooth pads'' found in ants\cite{RN201}, stick insects

\cite{RN182}, etc. and 2) ``hairy pads'' seen in flies \cite{RN155},

geckos \cite{RN202} and others. The hairy pads show: 1) compliance

to rough surfaces due to their lower effective modulus, 2) angle dependent

adhesion due to asymmetric hair geometry and 3) self-cleaning capability

\cite{RN20}, which makes them suitable to adhere to most surfaces

reversibly. Many of these insects pads also secrete an adhesive fluid,

as seen in flies and ants \cite{RN201} (``wet adhesion''), while

others such as spiders and geckos rely on their dry hairy pads for

attachment (``dry adhesion''). In the ``wet adhesion'' case, fluid

secretion can enforce adhesion through surface tension and viscous

forces \cite{RN71}, while, ``dry adhesion'' relies mostly on van

der Waals forces \cite{RN202}.

Terrestrial beetles such as the dock beetle or the ladybug have hairy

pads consisting of a dense array of hair-like structures called setae.

The setae tips can be discoidal, spatula or pointed shaped, which

are distributed throughout the pad depending on sex or species\cite{RN19}.

Single seta force measurements revealed that discoidal shaped seta

shows larger pull-off force than spatula and pointed setae\cite{RN79},

illustrating the role of hair geometry in adhesion. The tip of each

seta secretes approximately one femtoliter of oily adhesive fluid

\cite{RN108}. The fluid's chemical composition is identified as a

mixture of mostly long chain hydrocarbons\cite{RN96} with traces

of triglycerides, fatty acids and cholesterol\cite{RN221,RN222}.

A recent study by Gernay et. al.\cite{RN77}, based on an elastocapillary

model, has been able to reasonably predict single seta adhesion forces

theoretically, confirming the dominant role of surface tension in

the ``wet adhesion'' of beetles.

While most of the studies on insect adhesion are done under natural

conditions in air, insect attachment underwater has been relatively

unexplored. Typically, underwater adhesion is complicated to achieve

due to the difficulty in displacing the water layer and enable good

contact\cite{RN123}. Regardless, a study on leaf beetles\cite{RN87}

has revealed that they can in fact attach quite well to surfaces underwater.

Its hairy pad traps an air bubble underwater, which dewets the surface

on contact. It has been hypothesized that a combination of capillary

forces due the air bubble and hair van der Waals contact within the dewetted area

results in its adhesion underwater. However, a detailed investigation

of the bubble's contribution and necessity to adhere to different

surfaces is lacking. Geckos are also known to adhere underwater, where

its shear adhesion force on hydrophobic substrates are similar in

both air and underwater conditions. Interestingly, its adhesion on

a fluorinated substrate is even larger underwater than in air\cite{RN15}.

This has been partially explained by a thermodynamic work of adhesion

model, assuming full displacement of water at the interface, leading

to a dry ``van der Waals'' contact of hairs with the surface\cite{RN199}.

The goal of this paper is to provide a generalized picture of adhesion

~~in~~for insects which use hairy pads and secreting a fluid for attachment.

% Please check last sentence.

First, we ~~perform adhesion~~ measured adhesion of a single constrained pad

of a live ladybug beetle in air and underwater conditions, both on

smooth hydrophilic and hydrophobic glass surfaces, with a microscopic

observation of the contact process. Second, we develop a simple theoretical

model considering capillary forces to predict the net adhesion force

of a hairy pad under different conditions. Finally, we discuss key

insights gained from our experiments and model, as well as possible

implications in understanding adhesion in other animals.

\section{Experimental}

Normal adhesion force measurements on a restrained leg of a live ladybug

beetle were performed. We characterize adhesion by the pull-off force

during detachment. Measurements were done against smooth glass and

fluorinated surfaces to represent hydrophilic and hydrophobic substrates,

respectively. When no water was present, we labeled the contact type

as ``\emph{in air}''. For the underwater conditions, measurements

were done both in the presence and absence of a trapped bubble (``\emph{underwater:

bubble}'' and ``\emph{underwater: no bubble}'', respectively) to

investigate the bubble's role in underwater adhesion. Adhesions force

for each of the labeled contact types were compared for both substrates.

\subsection{Material and Methods}

\subsubsection{Insect preparation}

Seven-spotted male adult ladybug beetles (\emph{Coccinella septempuctata})

purchased from Katz Biotech (Baruth, Germany) were used for adhesion

tests. The beetles were housed in a plastic box filled with leaves,

twigs and stones at room temperature and 60-80\% relative humidity

with daily access to sunlight. They were fed with raisins, honey and

water\emph{ ad libitum}.

~~Experiments were done on male beetles.~~ Each leg of the beetle has

a pair of hairy pads covered with mostly discoidal shaped setae, capable

of strong adhesion. For the test, we only allowed the distal-end pad

to make contact. The beetle's leg was constrained similar to the method

described by Bullock et al \cite{RN19}. A steel ball fixed with a

piece of thick solder wire served as a rotatable holder to fix the

beetle and align its leg (Figure \ref{fig:Setup}). The beetle was

first anesthetized using CO\textsubscript{2} sublimating from a piece

of dry ice and then glued to the steel ball on its back. Its front

left leg was carefully fixed to the solder wire of the holder using

Blue-Tac. Its claws were fixed using epoxy glue to prevent any wiggling.

A small piece of non-sticky Teflon tape helped to keep its other legs

tucked close to the body and avoid their interference during the adhesion

test.

After measurements, the beetle was freed by carefully removing the

epoxy glue and Blue-Tac without harming it and set free.

\subsubsection{Substrate preparation}

Standard 20 mm wide glass coverslips were used as the hydrophilic

substrate. Glass was wiped with isopropanol, rinsed in water and dried

under nitrogen flow. The surface was then plasma cleaned in a oxygen

plasma chamber (Diener Electronic Femto) for 10 min at 120 W. The

surface was further rinsed with water and dried under nitrogen flow.

For the hydrophobic substrate, the glass cover slip was coated with

a fluorosilane via chemical vapor deposition (CVD). First, the glass

was cleaned using IPA and plasma treated as before. Next, 0.2 ml of

Trichloro(1H,1H,2H,2H-perfluorooctyl) silane (PFOTS), procured from

Sigma Aldrich, was put in a sealed chamber along with the the cleaned

glass. The chamber was placed under 100 mbar pressure for 10 min for

the CVD process. Finally, the substrate was annealed at 150\textcelsius{}

for 3 hours.

The substrate wettability was characterized by dynamic contact angle

measurements, performed with a DataPhysics OCA 35 contact angle goniometer.

De-ionized water and n-hexadecane were used as test liquids. Advancing

and receding contact angles were measured for a maximum drop volume

of 10 \textgreek{m}l and with 0.5 \textgreek{m}l/s flow rate~~. Static~~

~~contact angles were measured for a 5 \textgreek{m}l drop~~.

% What do we need static contact angles for?

\begin{table}[H]

\centering{}%

\begin{tabular}{|c|c|c|c|c|}

\hline

Substrate & Liquid & \ensuremath{\theta}\textsubscript{A} & \ensuremath{\theta}\textsubscript{R} & \ensuremath{\theta}\textsubscript{S}\tabularnewline

\hline

\hline

\multirow{2}{\*}{Glass} & Water & 63\ensuremath{\pm}5\textdegree{} & 20\ensuremath{\pm}2\textdegree{} & 57\ensuremath{\pm}2\textdegree{}\tabularnewline

\cline{2-5} \cline{3-5} \cline{4-5} \cline{5-5}

& n-Hexadecane & <10\textdegree{} & <10\textdegree{} & <10\textdegree{}\tabularnewline

\hline

\multirow{2}{\*}{PFOTS} & Water & 122\ensuremath{\pm}1\textdegree{} & 93\ensuremath{\pm}2\textdegree{} & 110\ensuremath{\pm}2\textdegree{}\tabularnewline

\cline{2-5} \cline{3-5} \cline{4-5} \cline{5-5}

& n-Hexadecane & 88\ensuremath{\pm}2\textdegree{} & 56\ensuremath{\pm}5\textdegree{} & 72\ensuremath{\pm}2\textdegree{}\tabularnewline

\hline

\end{tabular}\caption{Static and dynamic contact angles measurements \label{tab:Contact-Angles}}

\end{table}

\subsubsection{Field desorption mass spectroscopy}

Field Desorption Mass Spectrometry (FDMS) measurements of the adhesive

fluid secretions were performed using a ZAB 2-SE-FPD spectrometer (VG

Instruments). A previous study on archanids \cite{RN223} reported

that the secreted fluid does not dissolve ~~away~~ in water. To confirm

this for the beetle, measurements before and after the immersion of

its legs in water were done.

% I did not understand this part. Did you dissolve the legs? Only the remnanats on the glass, didn’t you?

The middle leg of an Asian ladybird (\emph{Harmonia

axyridis}) was immersed in 50 \textmu L THF for 20 min and then transferred

to the measurement chamber of the FDMS. As a reference, pure THF was

used. The second middle leg of the same ladybird was immersed in 100

\textmu L milli-Q water for 15 min, then in THF for 20 min and then

transferred to the measurement chamber of the spectrometer. Molecular

composition was extracted from the peak positions of the FDMS data.

\subsubsection{Adhesion test}

Adhesion measurements were performed on a custom force measurement

setup developed in-house (Figure \ref{fig:Setup}). A fiber optic

displacement sensor (\emph{Philtec D20, PHILTEC, Inc. USA}) together

with a steel bending beam (spring constant = 68.1 N/m) constitutes

the vertical force sensor. Beam deflection was calibrated using 4

different known weights to get the corresponding force. A plastic

3D printed substrate holder was glued to the end of the bending beam.

The holder was designed to enable switching from one substrate to

another without removing any glue. It also had transparent side walls

which allowed us to fill it with water for the underwater experiments

as well as observe the contact. The sensor was mounted on a stage

consisting of a X-piezo, used for precise lateral movements, XYZ motors,

for coarse movements and a goniometer, for adjusting substrate alignment

with the optics. Additionally, a separate Z-piezo, fixed upright,

was used for vertical up-down motion, bringing the insect in contact

with the substrate from the top. A 3 axis manual micro-manipulator

together with the rotatable steel ball allowed good alignment of the

beetle's foot to the substrate. A coaxial illuminated tube microscope

(\emph{Navitar}) with 2$\times$~~x~~ objective and a stereo-microscope with 1x

objective (\emph{Wild Heerbrugg}) fit with cameras were used to record

the sample contact with the substrate from ventral and side views

respectively. Pad contact area was visualized through the substrate

in total reflection mode by the ventral view camera. The data acquisition

from the force sensor and cameras, together with the appropriate piezo

motion steps were synchronized using a custom LABVIEW program. Force

data was acquired at a sample rate of 984 Hz, averaged to 512 points

per motion step. Videos were recorded at 20 frames per second.

The vertical and lateral piezos were together used to perform approach-retract

adhesion tests with the substrate to get the pull-off force. However,

instead of a simple down-up motion, some additional motion steps were

included (Figure \ref{fig:Setup}). A 100 \textgreek{m}m lateral sliding

motion was done after the leg makes contact, to give it a proximal

pull which will orient its hairs with the substrate \cite{RN19}.

An additional 10 \textgreek{m}m compression step (approach) was done

to ensure all hairs were loaded in compression and made good contact

with the surface. A short pause (1 s) was introduced to minimize any

viscoelastic effects before finally retracting the leg away from the

substrate. All approach, retract and lateral slide motion was done

at a speed of 62.5 \textgreek{m}m/s. Ventral view video recordings

were used for contact area extraction while the side view imaging

was used to visually aid orienting the pad with the substrate before

a test.

For underwater experiments, 1 ml MilliQ water was pipetted into the

substrate holder. In order to achieve an underwater contact without

a trapped air bubble, the water was first degassed in a vacuum chamber

at 10 mbar pressure for 3 hours and used immediately. Before experiment,

the pad was repeatedly brought into contact with the surface 10 times

to equilibriate the pad system. 5 force measurements were subsequently

performed on a fresh spot of the substrate and averaged for data analysis.

Experiments were repeated with 5 individual beetles for each type

of contact and substrate. In total, 30 beetles were tested.

\begin{figure}[H]

\begin{centering}

\includegraphics[scale=0.5]{Figure1-Setup\_schematic}

\par\end{centering}

\caption{\label{fig:Setup} Adhesion test setup. Representative force data

and contact area of distal pad are shown in the plot, in which, the

shaded regions represent distinct piezo motion steps, negative force

values represent attraction and the minimum force peak during the

final retraction step is the adhesion force.}

\end{figure}

\subsubsection{Data analysis}

Extraction of pull-off force from force data, image processing, plotting

and statistical analysis were all performed in ``\emph{Buggee}'',

a tool written in Python using open-source libraries for synchronous

analysis of force data and video recordings (\url{https://github.com/PranavSudersan/Buggee}).

For measurements in air, the pull-off force was defined as the minimum

negative force during the final retraction step. For underwater measurements,

an additional correction was necessary. When the beetle was submerged

underwater, its contact line at the water surface shifted, which influenced

the force readout due to surface tension effects. This effect needed

to be canceled. So, a ``background'' force data was recorded, where

the submerged beetle makes no contact with the substrate. This background

data was then subtracted from a typical force data with substrate

contact to correct for the external surface tension effects. The pull-off

force was subsequently calculated from the minima as before.

Data sets were compared for statistical differences using pairwise

Student t-test and their corresponding p-value and Common Language

Effect Size (CLES) are reported. Shapiro-Wilk test was done for each

data set to verify a normal distribution of its residuals and Levene's

test was done to check for variance homogeneity, to validate the t-test

assumptions. Bonferroni's correction was used to account for multiple

comparison between groups.

% Once you have decidied if Michjael or Thomas is corresponding authors, ask them if this paragraph is sufficient and necessary. I suggest to add for each test a half sentence telling the reader what they are good for. Are they necessary? All these tests may be reassuring but they assume statistical error. What about systematic artifacts?

% Shouldn’t we at some point describe a forces curve and how it was evaluated? We should certainly show at least one forxce curve. After all, that is the raw data.

\subsection{Results}

\subsubsection{Field desorption mass spectroscopy}

Molecular weights of the secreted fluid mixtures extracted from an

Asian ladybird's leg, dry~~without~~ and after immersion in water are compared

(Table \ref{tab:Molecular-distribution-of}). Except for two molecular

weights (406.8 g/mol and 331.6 g/mol), the chemical fingerprint remained

unchanged, indicating that the adhesion fluid was not washed away

underwater. Probable compounds in the fluid, corresponding to the

resultant molecular weights, include mostly aliphatic hydrocarbons

with traces of aldehydes.

\begin{table}[H]

\centering{}%

\begin{tabular}{|c|c|c|}

\hline

Without rinsing (g/mol) & After rinsing (g/mol) & Probable compounds\tabularnewline

\hline

\hline

324.5 & 324.5 & C\textsubscript{23}H\textsubscript{48}, C\textsubscript{22}H\textsubscript{44}O\tabularnewline

\hline

& 331.6 & C\textsubscript{24}H\textsubscript{44}\tabularnewline

\hline

350.5 & 350.5 & C\textsubscript{25}H\textsubscript{50}\tabularnewline

\hline

352.5 & 352.5 & C\textsubscript{25}H\textsubscript{52}, C\textsubscript{24}H\textsubscript{48}O\tabularnewline

\hline

378.5 & 378.5 & C\textsubscript{27}H\textsubscript{54}\tabularnewline

\hline

404.6 & 404.5 & C\textsubscript{29}H\textsubscript{56}\tabularnewline

\hline

406.8 & & C\textsubscript{29}H\textsubscript{58}\tabularnewline

\hline

432.8 & 432.7 & C\textsubscript{31}H\textsubscript{60}\tabularnewline

\hline

\end{tabular}\caption{Molecular weights of adhesive fluid secretion of \emph{Harmonia axyridis}

with and without rinsing the beetle's leg in water. Molecular weights

were extracted from the peaks in the FDMS spectra. \label{tab:Molecular-distribution-of}}

\end{table}

\subsubsection{Adhesion measurements}

Adhesion force of the distal pad of ladybug beetle against glass

and PFOTS in air and underwater conditions are compared (Figure \ref{fig:Effect-of-contact}

and Table \ref{tab:Statistical-analysis}). In air, there is no significant

difference in the adhesion force between glass and PFOTS substrate

(p = 0.959).

% This paragraph is important because it represent the core ouf your work. Furthermore, these two sentences are important, because they are the beginning of results. And they are confusing. They are confusing because you mention two pairs: glass/PFOTS and air/underwater. Who is compared with whom? Could you disentangle the two pairs? Here is one suggestion: “In air, adhesion forces of the distal pad of ladybug beetle against glass and PFOTS were rather similar; no significant differences were detected (Figure \ref{fig:Effect-of-contact}. In contrast, underwater…”

adhesion on a PFOTS surface wa~~i~~s significantly larger than on glass

(p < 0.001).

% This stronger adhesion on PFOTS surface was observed in the presence and absence of a trapped bubble. In both cases, adhesion force

o~~O~~n PFOTS reached the same values as~~, there is no significant difference in the adhesion~~

~~force~~ in air ~~or underwater conditions~~. In contrast, ~~But o~~On glass, adhesion underwater

was significantly reduced as compared to dry conditions, irrespective of the presence (p

= 0.002) or absence (p < 0.011) of a trapped bubble.

At the same, we see

that the presence of the bubble results in a higher adhesion force

than with no bubble (CLES = 0.84) on glass, although the difference

is not statistically significant (p = 0.07).

% The last sentence is a bit confusing. Do we think there is a difference or not? Suggestion: “In the presence of a bubble adhesion forces on glass tended to be slightly higher than without a bubble. However, this difference was small and not statistically significant (p = 0.07).

% I find all the p values and CLES confusing. Either table or text, but certainly not both. I would even suggest shifting the table to supporting Information. It does not seem to be essential.

\begin{table}[H]

\noindent \begin{centering}

\begin{tabular}{|>{\raggedright}m{0.15\linewidth}|>{\raggedright}m{0.15\linewidth}|>{\raggedright}m{0.15\linewidth}|>{\centering}m{0.15\linewidth}|>{\centering}m{0.15\linewidth}|}

\hline

Fixed & A & B & p-value & CLES\tabularnewline

\hline

\hline

In air & PFOTS & Glass & 0.959 & 0.48\tabularnewline

\hline

Underwater: bubble & PFOTS & Glass & 0.011 & 0.96\tabularnewline

\hline

Underwater: no bubble & PFOTS & Glass & \textbf{< 0.001} & 1.0\tabularnewline

\hline

PFOTS & In air & Underwater: bubble & 0.897 & 0.48\tabularnewline

\hline

PFOTS & In air & Underwater: no bubble & 0.828 & 0.48\tabularnewline

\hline

PFOTS & Underwater: bubble & Underwater: no bubble & 0.721 & 0.44\tabularnewline

\hline

Glass & In air & Underwater: bubble & \textbf{0.002} & 1.0\tabularnewline

\hline

Glass & In air & Underwater: no bubble & \textbf{< 0.001} & 1.0\tabularnewline

\hline

Glass & Underwater: bubble & Underwater: no bubble & 0.07 & 0.84\tabularnewline

\hline

\end{tabular}

\par\end{centering}

\caption{Pairwise statistical comparison of single leg adhesion force of the

beetle for each contact type and substrate. The uncorrected p-values

and Common Language Effect Size (CLES) are obtained from post-hoc

pair-wise Student t-test between A and B while keeping the third parameter

fixed. p-values showing statistically significant difference between

A and B are in boldface. The condition for statistical significance

is based on the Bonferroni-corrected critical p-value of 0.008.\label{tab:Statistical-analysis}}

\end{table}

\begin{figure}[H]

% As I said, I would shift the table to SI.

\centering{}\includegraphics[scale=0.5]{Figure2-Expt\_effect\_of\_contact}\caption{\label{fig:Effect-of-contact}Single leg adhesion force measurements

of ladybug beetle (\emph{Coccinella septempuctata}) on glass and PFOTS

substrates in air and underwater conditions. ~~Values represent peak~~

~~force of a distal pad pulled off from each substrate.~~ Three types

of contacts are seen in underwater experiments and are represented

separately: \textquotedblleft\emph{bubble}\textquotedblright , \textquotedblleft\emph{no

bubble}\textquotedblright{} and \textquotedblleft\emph{bad contact}\textquotedblright .

Crosses~~Stars~~ represent theoretical predictions of adhesion force calculated

from the capillary bridge model, where hair diameter = 4 \textgreek{m}m,

pad diameter = 200 \textgreek{m}m, hair height = 40 \textgreek{m}m,

N\protect\textsubscript{hairs} = 500, V\protect\textsubscript{fluid}

= 4.2 fL and V\protect\textsubscript{bubble} = 1.2 nL. Interfacial

tension of the adhesive fluid in air and water are assumed to be 24

mN/m and 48 mN/m respectively and water surface tension is 72 mN/m.}

\end{figure}

% This figure is the most important one but does not look great yet. At least in my printout. For example, the letters are much to small in proportion. What are the crosses and the bars?

Apart from the three predicted contact types, we ~~also~~ observed an

additional fourth type ~~of contact~~ which sometimes occur~~s~~ed underwater,

labeled as ``\emph{bad contact}''. In this scenario, the ventral

view recordings show that the hairs did not appear to contact well with

the substrate, unlike the other three contact types.

% Give a number instead of “sometime”, e.g. “In roughly ??? % of the cases…”. Furthermore, here we need a figure with pictures of the different contacts. You have pictures of the other three contacts (Figure 3). Why not this one?

``\emph{Bad

contact}'' shows no adhesion with either glass or PFOTS substrate.

While it was not completely clear why such a contact occurs, there can

be two possible reasons. First, the hairs could get bundled due to

a small air meniscus within the hairs, resulting in their disorientation.

Second, a thin water layer at the substrate interface might not be

drained out to allow the hairs to make contact with the substrate,

resulting in a loss of adhesion.

\section{Theory}

\subsection{Capillary Bridge Model}

We model the hairy pad as an array of $N$ cylindrical rods of length,

$L$, and diameter, $D\_{h}$, fixed to a flat circular pad of diameter,

$D\_{p}$ ( ~~as shown in figure~~ \ref{fig:Model}). The hairs and the pad

are assumed to be perfectly rigid, for simplicity. The tip of each

hair has an adhesive fluid of volume, $V\_{f}$, making contact with

the substrate. The fluid is pinned to the circumference of the hair

and forms a capillary bridge of height, $d$. Similar to our experiments,

we consider three types of contacts for the pad: 1) \emph{In air},

2) \emph{Underwater: no bubble} and 3) \emph{Underwater: bubble}.

In the third case, a bubble of volume, $V\_{b}$, is trapped between

the hairs and pinned to the pad circumference.

\begin{figure}[H]

\includegraphics[width=0.7\linewidth]{Figure3-Model\_schematic}\caption{\label{fig:Model}The capillary bridge model. The hairs make contact

with the substrate in three ways: a) \emph{In air}, where the adhesive

fluid bridges are surrounded by air; b) \emph{Underwater: no bubble},

where the adhesive fluid bridges are fully surrounded by water; c)\emph{

Underwater: bubble}, where part of the adhesive fluid bridges are

inside the bubble while others are outside in water. The corresponding

ventral view contact images of the beetle's pad are shown on the right.}

\end{figure}

To characterize the adhesive fluid and bubble volume we define two radii, $s\_f$ and $s\_b$, respectively, by $V\_{f}=\frac{4}{3}\pi s\_{f}^{3}$ and $V\_{b}=\frac{4}{3}\pi s\_{b}^{3}$.

Here, $s\_{f}$ and $s\_{b}$ are the radii of spheres with equivalent

volumes. Fluid and bubble radii are assumed to scale proportional

to their corresponding pinned contact diameter. We thus defined the

size parameters, $\phi\_{f}=D\_{h}/\left(2s\_{f}\right)$ and $\phi\_{b}=D\_{p}/\left(2s\_{b}\right)$

for the fluid and bubble respectively, to conveniently scale their

volumes relative to the hair and pad diameters they were pinned to.

The net force for cases 1 and 2 can be calculated as:

\begin{equation}

F\_{net}=Nf\label{eq:f\_air/water}

\end{equation}

Here, $f$ is the capillary force of a single fluid bridge at a distance,

$d$, in air ($f\_{air}$) or underwater ($f\_{water}$).

For case 3, the net force is given by:

\begin{equation}

F\_{net}=N\_{in}f\_{air}+N\_{out}f\_{water}+f\_{bubble}\label{eq:f\_bubble}

\end{equation}

Here, $N\_{in}$ and $N\_{out}$ are the number of hairs inside and

outside the bubble, respectively, $f\_{air}$ and $f\_{water}$ are

the capillary forces of the fluid bridge inside and outside the bubble,

respectively, and $f\_{bubble}$ is the capillary force contribution

due to the bubble meniscus alone at distance $d+L$.

The capillary force, $f$, is the sum of two contributions: surface

tension and Laplace pressure. Force versus distance for a single capillary

bridge is calculated by Surface Evolver simulations\cite{RN206},

(described in \ref{subsec:Simulation-Method}) and used to obtain

$F\_{net}$ as a function of $d$ for each type of contact. The adhesion

force of the complete hairy pad system is then obtained from the minima

of $F\_{net}$, where negative force values represent attraction.

We have considered $f\_{air}$ and $f\_{water}$ to be distinct terms

because the capillary force by the adhesive fluid will be different

in air and underwater due to its different contact angle and interfacial

tension in each case. Using the Young-Dupr\textcyr{\`\cyre} equations,

one can derive the following relation for the contact angle of the

adhesive fluid underwater:

% For my taste this should be better explained. How do you reach Eq. (3)?

\begin{equation}

\cos\theta\_{fw}=\frac{\gamma\_{fa}\cos\theta\_{fa}-\gamma\_{wa}\cos\theta\_{wa}}{\gamma\_{fw}}\label{eq:theta\_fw}

\end{equation}

Here, $\theta\_{fw}$ and $\theta\_{fa}$ are the contact angles of

the adhesive fluid with the substrate in water and air respectively,

$\theta\_{wa}$ is the contact angle of water with the substrate in

air, $\gamma\_{fa}$ is the surface tension of the adhesive fluid,

$\gamma\_{wa}$ is the surface tension of water and $\gamma\_{fw}$

is the interfacial tension of the adhesive fluid with water.

All lengths are normalized w.r.t. $s\_{f}$ and forces are normalized

w.r.t. $\gamma\_{fa}s\_{f}$. Interfacial tension values are fixed relative

to $\gamma\_{fa}$. Non dimensional bubble volume is expressed as,

$\hat{V}\_{b}=V\_{b}/s\_{f}^{3}$

Geometric parameters and interfacial properties are kept fixed for

all model calculations (Table \ref{tab:Model-parameters}). Here,

we assume the adhesive fluid to be an oil-lke substance and thus the

interfacial tension ratios $\gamma\_{wa}/\gamma\_{fa}$ and $\gamma\_{fw}/\gamma\_{fa}$

are taken corresponding to typical values of oil and water. We consider

representative hydrophilic and hydrophobic substrates with $\theta\_{fa}$

and $\theta\_{wa}$ values corresponding to a typical glass and fluorinated

surface, respectively. Area fraction of the hairs relative to the

pad, $\alpha=ND\_{h}^{2}/D\_{p}^{2}$, hair aspect ratio, $L/D\_{h}$,

and fluid size parameter, $\phi\_{f}$, are fixed to values typical

for a ladybug's hairy pad.

First, we calculate force-distance curves for a single pinned liquid

capillary bridge. Second, the effect of substrate on the force-distance

curves of the hairy pad system is compared for each type of contact.

Third, the effect of varying hair diameter, $D\_{h}$, on net adhesion

is studied. Finally, we look at the effect of changing the bubble

volume, $\hat{V}\_{b}$, on the net underwater adhesion.

% Did you give arguments why you chose the parameters in the given way? For example why did you chose these particular surface tensions? Which volume of the adhesion fluid did you chose?

\begin{table}[H]

\centering{}%

\begin{tabular}{|l|c|}

\hline

Property & Value\tabularnewline

\hline

\hline

Area fraction, $\alpha$ & 0.1\tabularnewline

\hline

Hair aspect ratio, $L/D\_{h}$ & 10\tabularnewline

\hline

Water surface tension ratio, $\gamma\_{wa}/\gamma\_{fa}$ & 3\tabularnewline

\hline

Fluid-water interfacial tension ratio, $\gamma\_{fw}/\gamma\_{fa}$ & 2\tabularnewline

\hline

Fluid size parameter, $\phi\_{f}$ & 2\tabularnewline

\hline

Hydrophilic substrate & $\theta\_{fa}=6\lyxmathsym{\textdegree}$, $\theta\_{wa}=24\lyxmathsym{\textdegree}$\tabularnewline

\hline

Hydrophobic substrate & $\theta\_{fa}=50\lyxmathsym{\textdegree}$, $\theta\_{wa}=120\lyxmathsym{\textdegree}$\tabularnewline

\hline

\end{tabular}\caption{\label{tab:Model-parameters}Fixed parameters of the capillary bridge

model}

\end{table}

~~\subsection{Results}~~

% I find two results section confusing

\sub~~sub~~section{Capillary force of a pinned liquid bridge\label{subsec:Capillary-force-of}}

Forces due to a single pinned capillary liquid bridge in contact with

a substrate are obtained via Surface Evolver simulations (Figure \ref{fig:Single-bridge}).

% Shouldn’ t we say how you determined the Laplace pressure and the direct action of the capillary force?

Capillary forces are more attractive for smaller contact angles. The

Laplace pressure contribution to the net adhesion force dominates

for contact angles less than 100\textdegree{} (Figure \ref{fig:Single-bridge}b).

Interestingly, its contribution to the adhesion force is mostly non-repulsive

for contact angles greater than 90\textdegree . This is because, the

low volume of the liquid and its pinned contact line prevents the

meniscus from having a high positive curvature due to geometric constraints.

Only for a contact angle of 150\textdegree , the liquid's curvature

becomes positive, manifested in its slightly repulsive Laplace contribution.

Surface tension makes a significant contribution to the net force

only for a small range of contact angles close to 90\textdegree .

For contact angles greater than 150\textdegree , the net adhesion

force approaches zero. We see that, generally, the shape of the liquid

meniscus determines the strength of its adhesion force. High adhesion

is thus seen for contact angles less than $\sim$ 70\textdegree{}

due to a net negative curvature of the meniscus, while low adhesion

is seen for contact angles greater than $\sim$ 150\textdegree{} due

to its net curvature being close to zero.

% I suggest shifting the red part up. You start the paraghraph with the least important results (That The Laplace pressure is positive for…) and end with the most important part (Strong adhesion at low CA). That does not fit. Reverse it. Then you can even end you paragraph with an interesting surprise.

\begin{figure}[H]

\begin{minipage}[t]{0.5\columnwidth}%

\includegraphics[scale=0.5]{Figure4a-Single\_bridge\_fd}

\subcaption{Force-distance curves}%

\end{minipage}\hfill{}%

\begin{minipage}[t]{0.5\columnwidth}%

\includegraphics[scale=0.5]{Figure4b-Single\_bridge\_force\_contribution}

\subcaption{Force contributions}%

\end{minipage}\caption{\label{fig:Single-bridge}Normalized capillary force of a single liquid

bridge in contact with a substrate and pinned to a circular perimeter

on top. Fluid size parameter, $\phi\_{f}=2$. Negative force values

represents attraction. a) Force-distance curves are shown for different

contact angles of the liquid with the substrate. b) Adhesion forces,

calculated from the minima of the corresponding force-distance curves,

are~~is~~ plotted as a function of contact angle with the substrate, together

with its Laplace and surface tension components (equation \ref{eq:f\_bridge}).

Simulation snapshots of the liquid meniscus corresponding to angles

6\textdegree{} and 150\textdegree{} are depicted.}

\end{figure}

The force-distance curves show a general trend of being repulsive

at small distances (Figure \ref{fig:Single-bridge}a). This is a result

of the pinned contact line on the top. A limited volume is available

for the liquid to occupy when the gap distance is small, causing the

meniscus shape to bulge outwards near the pinned contact line. This

creates a net positive curvature, resulting in a positive Laplace

pressure and thus repulsion.

% What if you allow the meniscus to slide up on the pillar at constant advancing CA? This would be the natural thing to happen and would get rid of this repulsive part. I suggest that you at least mention this case. Otherwise people with strange experimental results might use you theoretical results to support their own strange results.

\sub~~sub~~section{Capillary Bridge Model: Effect of the substrate\label{subsec:Capillary-Bridge-Model:}}

% let me only make one general comment with resepct to this subsection: Make it more a story rather than a report. More a chain of arguments and results rather than a list.

The normalized force-distance curves of a hairy pad system on a hydrophilic

and hydrophobic substrate are predicted based on the capillary bridge

model and compared for the different contact types (Figure \ref{fig:Effect-of-substrate}).

The forces in each case are calculated from equations (\ref{eq:f\_air/water})

and (\ref{eq:f\_bubble}) for fixed geometric and interfacial properties

(Table \ref{tab:Model-parameters}).

On the hydrophilic substrate ($\theta\_{wa}=24\lyxmathsym{\textdegree}$),

contact\emph{ in air} shows the highest adhesion. \emph{Underwater:

no bubble} shows close to no adhesion while \emph{underwater: bubble}

shows moderate adhesion. In contrast, for a hydrophobic substrate

($\theta\_{wa}=120\lyxmathsym{\textdegree}$), the highest adhesion

is seen for \emph{underwater: no bubble}, much larger than \emph{in

air}. Even \emph{underwater: bubble} has slightly higher adhesion

than \emph{in air}. Note that the contact area is fixed by keeping

the area fraction and $D\_{p}/D\_{h}$ constant. All curves correspond

to the same total hair contact area. Thus, the above mentioned effects

are attributed solely to how the the capillary force changes in each

scenario.

On a hydrophilic substrate, the contact angle of the oily adhesive

fluid is 6\textdegree , when surrounded by air (Table \ref{tab:Model-parameters})

and 150\textdegree , when surrounded by water (equation (\ref{eq:theta\_fw})).

This results in the meniscus shape to have a net negative and slightly

positive curvatures, respectively, resulting in strong adhesion in

air and poor adhesion underwater. On a hydrophobic substrate however,

the contact angles of the fluid in air and water are 50\textdegree{}

and 1\textdegree , respectively. In both cases, the contact angles

are low, resulting in strong adhesion in both media. Additionally,

the interfacial tension of the oily fluid underwater ($\gamma\_{fw}$)

is twice that of in air ($\gamma\_{fa}$). Thus, we see a higher capillary

adhesion for the \emph{underwater: no bubble} case when compared to

\emph{in air} (Figure \ref{fig:Oil-contact-images}).

\begin{figure}[H]

\centering{}\includegraphics{Figure5-Model\_effect\_of\_substrate}\caption{\label{fig:Effect-of-substrate}Theoretical force-distance curves

of a hairy pad system on a hydrophilic and hydrophobic substrate in

air and underwater conditions. A negative force value represents attraction.

Normalized forces are calculated from the capillary bridge model,

with model parameters listed in Table \ref{tab:Model-parameters}.

The bubble's contribution to the net force for an \emph{underwater:

bubble} contact is denoted by plus symbols. Insets represent the \emph{underwater:

bubble }contact for each substrate.}

\end{figure}

The net force in the \emph{underwater: bubble} case mainly depends

on the proportion of hairs inside and outside the bubble (equation

(\ref{eq:f\_bubble})). For the given bubble volume, only part of the

hairs are inside the bubble for the hydrophilic substrate, while,

all the hairs are inside the bubble for the hydrophobic substrate.

Therefore, the force curve lies between \emph{in air} and \emph{underwater:

no bubble} cases for a hydrophilic substrate, and closely follows

the \emph{in air} case for a hydrophobic substrate.

The contribution of the capillary force due to the bubble itself is

negligible for both substrates (Figure \ref{fig:Effect-of-substrate}).

Its contribution even is slightly repulsive on the hydrophilic substrate

due to the positive curvature of the bubble, and slightly attractive

on the hydrophobic substrate due to its negative curvature. This small

contribution is manifested by the slightly higher adhesion for \emph{underwater:

bubble} relative to \emph{in air} for the hydrophobic substrate, since

all hairs are within the bubble in this case.

\sub~~sub~~section{Capillary Bridge Model: Effect of bubble volume}

% I am missing somehow a motivation. Why shoud I care about the bubble size? This should be mentioned either in the introduction or here. Suggestion: Since ladybirds bring air bubbles on their toe pads into water the question arises, if these air bubbles influence the adhesion? More general: How does the size of an air bubble influence adhesion of toe pads to surfaces?

The effect of varying bubble volume, $\hat{V}\_{b}$, on the net adhesion

force of the \emph{underwater: bubble} case are compared for hydrophilic

and hydrophobic substrates (Figure \ref{fig:Effect-of-bubble}). From

previous section, we know that on the hydrophilic substrate, fluid

bridges outside the bubble show poor adhesion due to the positive

curvature of their meniscus. Thus, decreasing $\hat{V}\_{b}$ decreases

the adhesion force due to a larger proportion of hairs being outside

the bubble. In contrast, on the hydrophobic substrate, fluid bridges

outside the bubble show higher capillary forces, due to its low contact

angle and high interfacial tension in water.

% I suggest first giving the results and then the interpretation. Describing the expectation maybe OK, but summarizing the results only in the last sentence does not seem appropriate to me. We only confirm what one could have known anyways.

Thus, adhesion force

increases for a hydrophobic substrate as the bubble size decreases.

\begin{figure}[H]

\includegraphics{Figure7-Model\_effect\_of\_bubble\_volume}\caption{\label{fig:Effect-of-bubble}Normalized adhesion force of a hairy

pad system as a function of bubble volume, $\hat{V}\_{b}$, for the

\emph{underwater: bubble} contact type. Adhesion forces are calculated

from the minima of the respective force-distance curves. Negative

force value represents attraction. Pad to hair diameter ratio ($D\_{p}/D\_{h}$)

is kept fixed. Highlighted regions represent entrapment of all hairs

within the bubble.}

\end{figure}

The contribution of the bubble to the net adhesion force is small

regardless of its volume, when compared to the whole pad. We see that

a smaller $\hat{V}\_{b}$ results in increased attraction by the bubble

on both types of substrates. For larger values of $\hat{V}\_{b}$,

the force trend for the whole pad mostly follows that of the bubble,

because the bubble in this case is big enough to entrap all the hairs

inside it. Thus, the force contribution due to the fluid bridges remain

unchanged, and only the bubble's contribution drives the slight variation

in the pad's adhesion at high $\hat{V}\_{b}$. Once the bubble is small

enough such that part of the fluid bridges start making contact in

water, the force trend changes, with a steep decrease (increase) in

adhesion force on hydrophilic (hydrophobic) substrate as the volume

decreases.

\sub~~sub~~section{Capillary Bridge Model: Effect of hair diameter }

The effect of changing hair diameter, $D\_{h}$, to the net adhesion

force is compared for hydrophilic and hydrophobic substrates (Figure

\ref{fig:Effect-of-hair}).

% Again, this sentence may be confusing. Are you describing the effect of radius or do you focus on comparing hydrophilic and hydrophobic surfaces? Separate both aspects.

Here, the pad diameter, total hair contact

area and bubble volume are constant since $D\_{p}$, $\alpha$ and

$\hat{V}\_{b}$ are kept fixed. The radius corresponding to the fluid

volume is assumed to scale proportional to the hair diameter and is

fixed ($\phi\_{f}=2$).

Adhesion force increases with decreasing $D\_{h}$ for both hydrophilic

and hydrophobic substrates in all contact types. This is consistent

with the ``contact splitting'' theory, which predicts higher adhesion

when the contact is split into many small contact points\cite{RN24}.

Reducing the hair diameter results in two competing effects: 1) capillary

force due to a single fluid bridge decreases due to its smaller size

and ``self-similar'' scaling assumption ($f\sim D\_{h}$), which

decreases the net force, and 2) total number of fluid bridges increases

since the total hair contact area is assumed to be fixed ($N\sim1/D\_{h}^{2}$),

which increases the net force. The second effect dominates, resulting

in a higher adhesion force as $D\_{h}$ decreases.

\begin{figure}[H]

\includegraphics[scale=0.5]{Figure6-Model\_effect\_of\_hair\_size}\caption{\label{fig:Effect-of-hair}Normalized adhesion force of a hairy pad

system on a hydrophilic and hydrophobic substrate as a function of

hair diameter, $D\_{h}$. Volume of each fluid bridge, $V\_{f}$, scales

relative to $D\_{h}$ based on the parameter $\phi\_{f}=2$. Adhesion

forces are calculated from the minima of the respective force-distance

curves, based on the capillary bridge model. A negative value represents

attraction. The bubble's contribution to the net force for an \emph{underwater:

bubble} contact is denoted by plus symbols. Pad diameter and bubble

volume are kept fixed. All lengths are scaled relative to $D\_{p}$.}

\end{figure}

Similar to the trend in Figure \ref{fig:Effect-of-substrate}, contact

\emph{in air} shows the highest adhesion force on a hydrophilic substrate

for the given range of hair diameters, while on a hydrophobic substrate,

\emph{underwater: no bubble} shows highest adhesion. \emph{Underwater:

bubble} contact shows intermediate adhesion between \emph{in air}

and \emph{underwater: no bubble} contact types.

The bubble's contribution gets repulsive as hair diameter decreases

for both substrates (Figure \ref{fig:Effect-of-hair}). Since the

aspect ratio $L/D\_{h}$ is fixed (Table \ref{tab:Model-parameters}),

decreasing the hair diameter also decreases its length. Since the

bubble's volume is kept constant, it will then have a lesser space

available to occupy between the pad and the substrate, This results

in it bulging outwards near the pinned contact line on the top. Thus,

the bubble's contribution gets repulsive as hair diameter decreases.

\section{Discussion}

Our experiments demonstrate~~, for the first time,~~

% After reading the introduction that should be clear. Otherwise, change the introduction.

that the ladybug

beetle can attach underwater to a hydrophobic substrate even without

a bubble trapped around its hairs. A previous study\cite{RN87} had

hypothesized that a bubble is necessary for underwater attachment

in beetles. This is, however, only true for hydrophilic substrates,

where a trapped bubble can facilitate underwater adhesion due to the

hairs making contact in a dewetted environment. For a hydrophobic

substrate, the adhesion is similar regardless of whether the contact

occurs in air or underwater conditions, with or without a trapped

bubble.

% I would shift this part in the introduction. Then you can easily motivate your work. Until here, the reader may ask: Why do they care about bubbles and bubble size? If you shift this part to the intro, that question is gone.

Our theoretical calculations further show that the bubble

by itself has a negligible capillary contribution to the net underwater

adhesion of the pad. Direct force measurement of a single similarly

sized bubble making contact with a hydrophobic substrate shows a maximum

adhesion less than 50 \textgreek{m}N, which further validates that

the bubble's contribution is insignificant (\ref{subsec:Capillary-force-due}).

Predictions of the ladybug's adhesion from the capillary bridge model

agree with~~follow~~ our experimental results (Figure \ref{fig:Effect-of-contact}).

In underwater conditions without a trapped bubble, adhesion on a hydrophobic

substrate is significantly larger than on a hydrophilic substrate.

This is explained by the different oil interfacial tension and contact

angles with the substrates in air and underwater, which determines

the capillary adhesive force in each case (Figure \ref{fig:Oil-contact-images}).

However, the experiments don't show the predicted $\sim$ 2.6 times

increase in underwater adhesion relative to that in air on the hydrophobic

PFOTS surface. This discrepancy could be due to our assumptions of

the oily fluid's interfacial properties. If we choose $\gamma\_{fa}$=30

mN/m and $\gamma\_{fw}$=40 mN/m, the corresponding increase in adhesion

will be $\sim$ 1.7, closer to our experimental value of $\sim$ 1.

The resulting change in $\theta\_{fa}$ and $\theta\_{fw}$ will further

decrease this number. Direct measurement of the fluid's interfacial

properties is thus essential to better predict the insect's adhesion,

and will be a subject of future study. Further, due to surface inhomogeneities,

not all the hairs might be able to completely drain the interfacial

water layer, in order for the adhesive fluid to make a direct contact

with the substrate. This can further reduce underwater adhesion, in

comparison to our theoretical predictions which assumes a perfect

contact.

\begin{figure}[H]

\includegraphics{Figure-8-contact\_angle\_schematic}\caption{\label{fig:Oil-contact-images}Simulation snapshots of oil capillary

meniscus in contact with glass and PFOTS in air and underwater conditions.

The corresponding interfacial tension, \textgreek{g}, and contact

angle, \ensuremath{\theta}, used to predict the ladybug's adhesion

are labeled for each case.}

\end{figure}

% Why do you show these simulations here and not in the theory, results section?

In the model, we assume that all the hairs detach simultaneously to

give a theoretical maximum achievable adhesion force. In our experiments,

however, the pad always makes contact with the substrate at a random

orientation, which is difficult to control precisely. During detachment,

the pad typically peels off from its proximal to distal end rather

than detach simultaneously. Our model also assumes the hairs to be

of similar geometry, unlike the beetle's pad which has a distribution

of flat or pointed tipped hairs. Thus, it's not surprising that the

model overestimates the adhesion forces. The predictions are however

in the same order of magnitude as experiments, and the qualitative

trend is consistent for both hydrophilic and hydrophobic substrates

in air and underwater.

Our study provides further validation that capillary forces by the

adhesive fluid control the insect's adhesion and van der Waals contribution,

if any, must be negligible. Further, the capillary forces can even

enable insect attachment underwater depending on the substrate chemistry.

When underwater, without a trapped bubble, the pad adheres strongly

to a hydrophobic substrate, but poorly to a hydrophilic substrate,

even though it shows similarly strong adhesion to both substrates

in air. This behavior can only be explained by capillary forces. Our

preliminary FDMS results further provides validation to our assumption

that the adhesive fluid can form capillary bridges with the substrate

in water, instead of getting washed away (Table \ref{tab:Molecular-distribution-of}).

The findings can also be extended to other animals relying on oily

secretions for adhesion. Ants, for example, show similar adhesion

on hydrophobic substrates under wet and dry conditions\cite{RN213},

similar to what we see in a ladybug. Recent adhesion experiments on

geckos reveal that they can attach well to fluoropolymer substrates

underwater while they show little adhesion to the same substrate in

air\cite{RN199,RN15}. Geckos are thought to rely on van der Waals

forces via dry contact with the substrate \cite{RN202}, although

recent observations of phospholipid footprints left behind walking

geckos \cite{RN205} could change that picture. Since geckos adhere

poorly to PTFE (surface energy \textasciitilde{} 20 mN/m) one can

speculate that the phospholipid material has a higher surface energy,

and consequently makes a higher contact angle with PTFE in air. Let

us assume the phosopholipid substance to be a fluid similar to oil

with $\gamma\_{fa}$= 30 mN/m and $\gamma\_{fw}$= 42 mN/m such that

its contact angle with PTFE is 80\textdegree . Equation \ref{eq:theta\_fw}

then gives us an underwater contact angle of 70\textdegree{} for the

phospholipid fluid. Thus, on a PTFE surface, the capillary bridge

model can predict a higher adhesion underwater than in air due to

its lower contact angle and higher interfacial energy underwater.

Based on similar assumptions, we predict the net adhesion force for

the gecko on different substrates (Figure \ref{fig:Comparison-with-model}).

The adhesion force predictions are in good qualitative agreement with

the whole animal experimental shear force values reported for the

gecko, with the trend of higher adhesion in air than underwater for

glass, similar adhesion in air and underwater for PMMA/OTS-SAM and

lower adhesion in air than underwater for PTFE. We, thus, propose

that the underwater experiments performed on geckos \cite{RN199,RN15}

indicate a capillary contribution to gecko adhesion. We suggest performing

single seta adhesion force tests similar to Autumn et. al. \cite{RN202}

using a hydrophilic and fluorinated probe in air and underwater conditions

to validate the role of capillary contributions to gecko adhesion.

\begin{figure}[H]

\includegraphics{Figure-9-Gecko\_comparison}\caption{\label{fig:Comparison-with-model}Whole animal adhesion force of geckos

on various substrates. Experimental shear adhesion values are reproduced

from Stark et. al. \cite{RN15}. Normal adhesion forces for each gecko

toe are theoretically estimated from the capillary bridge model, with

hair diameter = 400 nm, toe diameter = 4 mm, adhesive fluid volume

= 4.19x10\protect\textsuperscript{-3} fL and 10\% hair coverage.

\textquotedblleft\emph{Underwater: no bubble}\textquotedblright{}

type contact is assumed for the \textquotedblleft Wet\textquotedblright{}

case. Net adhesion force is calculated by assuming 5 toes on each

leg and 4 legs in total on a gecko. Interfacial tension of the phospholipid

layer (PL) in air and water are assumed to be 30 mN/m and 42 mN/m

respectively. PL contact angles with glass, PMMA, OTS-SAM and PTFE

are assumed to be 6\textdegree , 10\textdegree , 20\textdegree{} and

80\textdegree{} respectively. The corresponding water contact angles

are 50\textdegree , 85\textdegree , 94\textdegree{} and 97\textdegree{}

respectively, as reported in Stark et. al. \cite{RN15}.}

\end{figure}

We have so far limited our analysis to only smooth substrates. Insects

in the real world, however, interact with rough substrates very often.

Previous studies \cite{RN136} have shown that substrate roughness

is a more dominant parameter than substrate chemistry in controlling

insect adhesion. Future work will explore how roughness can impact

the net capillary force. Our study can have potential applications

in the design of bio-inspired materials to achieve underwater adhesion

via capillary bridges. Bubble can possibly be used to control underwater

adhesion by changing the relative proportion of the arrays inside

and outside the bubble. A suitable choice of adhesive fluid can be

made tailored to the substrate and environment of application to achieve

optimal adhesion performance.

\section{Conclusions}

~~Our study illustrates that the L~~adybug beetles rely~~ies~~ primarily on

its oily fluid secretion to ~~achieve~~ adhere to surfaces in both air and underwater

conditions. The beetle can attach underwater on a hydrophobic substrate

even without a trapped air bubble within its hairy pad, although it

loses this ability on a hydrophilic substrate. This is explained theoretically

by the different contact angle and interfacial tension of the adhesive

fluid in air and underwater conditions. Further, the bubble itself

has a negligible capillary contribution to the total force. The trapped

bubble can promote adhesion only on a hydrophilic substrate by providing

an air medium to the adhesive fluid bridges inside it. Oil wettability,

thus, primarily controls the insect's adhesion in any given condition.

A similar argument also explains previously reported underwater measurements

in geckos \cite{RN15}, which highlights the possibility of capillary

contributions to gecko adhesion. Future studies should characterize

the fluid secretion's interfacial properties with a particular substrate

to better understand the nature of the animal's adhesion.

\section{Acknowledgement}

We are grateful to Eduard Arzt and Ren\textcyr{\`\cyre} Hensel for

fruitful discussions. This work was funded by \emph{Deutsche Forschungsgemeinschaft}

(Grant number: PI 1351/2-1).

\appendix

\section{Appendix}

\subsection{Simulation method: Single capillary bridge \label{subsec:Simulation-Method}}

\setcounter{figure}{0} \renewcommand{\thefigure}{A.\arabic{figure}}

\setcounter{equation}{0} \renewcommand{\theequation}{A.\arabic{equation}} Capillary

force due to a single adhesive fluid or bubble meniscus (termed ``capillary

bridge'') is calculated by performing simulations in Surface Evolver

\cite{RN206}, similar to the method described by De Souza et. al.\cite{RN93}.

A simple cubic geometry, mimicking the capillary bridge, of constant

volume, $V$, is defined as the initial condition with an interfacial

tension, $\gamma$, with the surrounding medium. Interfacial tension

of the capillary bridge with the substrate is given by $\gamma\cos\theta$,

where $\theta$ is the corresponding contact angle inside the bridge.

For the case of a bubble meniscus, $\theta$ is defined w.r.t. the

surrounding water, since $\theta$ can also directly characterize

the substrate wettability. The capillary bridge spans a gap distance

$d$ between the top face and the substrate. The boundary conditions

are set corresponding to a pinned contact line of diameter $D$ on

the top face and constant interfacial tension with the substrate on

the bottom. All lengths are normalized relative to length $s=\left(3V/4\pi\right)^{1/3}$.

An appropriate geometry refinement routine is chosen to evolve the

capillary bridge shape to its minimum energy state. The normalized

total capillary force, $\hat{f}=f/\gamma s$, is the sum of the Laplace

pressure and surface tension contributions , where:

\begin{equation}

f=f\_{laplace}+f\_{surface\,tension}=\varDelta P\_{laplace}A\_{\_{bottom}}+2\pi R\_{bottom}\gamma\sin\theta\label{eq:f\_bridge}

\end{equation}

Here, $\varDelta P\_{laplace}$ is the Laplace pressure of the equilibrium

capillary bridge, $A\_{bottom}$ is the contact area of the capillary

bridge with the substrate at bottom and $R\_{bottom}$ is the corresponding

radius of contact, all obtained from the simulation output for the

equilibrium surface.

The gap distance $d$ is varied stepwise and the capillary force is

calculated each time to obtain force-distance curves for a particular

choice of $D$ and $\theta$.

\subsection{Single capillary bridge: Effect of volume}

Surface Evolver simulation results showing the effect of volume on

the maximum capillary force of a single fluid bridge. Since the fluid

is pinned at the top to the same diameter, D, a smaller volume would

result in high interfacial curvatures, which increases the capillary

force due to the negative Laplace pressure. In this case, small contact

angles lead to a greater increase in adhesion.

\begin{figure}[H]

\begin{centering}

\includegraphics{FigureS2-Effect\_of\_fluid\_volume}\caption{Normalized maximum capillary force for a single bridge as a function

of fluid volume}

\par\end{centering}

\end{figure}

\subsection{Capillary Bridge Model: Effect of hair diameter at constant fluid

volume}

Here, instead of scaling the fluid volume relative to the hair diameter,

we now assume a fixed total fluid volume distributed equally among

the $N$ hairs. Total fluid volume, $V\_{total}=NV\_{f}=2000$. Hair

diameter is varied while keeping the total hair contact area constant.

Length is in arbitrary units. Forces increase at a much smaller rate

on decreasing diameter when compared to the case with self-similar

scaling of fluid volume (Figure \ref{fig:Effect-of-hair}).

\begin{figure}[H]

\includegraphics{FigureS3-Effect\_of\_hair\_size(constant\_vol)}

\caption{Normalized adhesion force of hairy pad system on a hydrophilic and

hydrophobic substrate as a function of hair diameter ($D\_{h}$), calculated

from the capillary bridge model. The total adhesive fluid volume is

fixed to 2000. Adhesion forces are calculated from minima of the respective

force-distance curves. Negative force value represents attraction.

The bubble's contribution to the net force for an \emph{underwater:

bubble} contact is denoted by plus symbols. Bubble volume and pad

diameter are kept fixed. All lengths are scaled relative to $D\_{p}$.}

\end{figure}

\subsection{Capillary force due to a bubble\label{subsec:Capillary-force-due}}

Capillary force of a single bubble against a PFOTS surface are compared

for two different volumes. The volumes correspond to the expected

range in the case of the trapped bubble in a ladybug. Here, the bubble

is pinned to a micropatterned PDMS substrate on the top. The maximum

adhesion force of any of the bubble never exceeds 50 \textgreek{m}N,

significantly lower than the beetle's underwater adhesion to the same

substrate (> 400 \textgreek{m}N). Thus, the bubble's contribution

to adhesion in the ``\emph{underwater: bubble}'' contact of a ladybug's

pad should be negligible.

\begin{figure}[H]

\begin{centering}

\includegraphics{FigureS4-Expt\_bubble\_force}\caption{Capillary force of the bubble}

\par\end{centering}

\end{figure}

\bibliography{references}

\end{document}