Porous superhydrophobic membranes as safe bubble absorbers for hydrocarbon industry

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Abstract. Superhydrophobic surfaces, which repels water droplets falling on them is a hot topic in the interfacial engineering for their wide range of applications from self-cleaning to thermal management. Recently, porous superhydrophobic surfaces are introduced to the front by incorporating the element of diffusion of gases along with the extreme non-wettability of the surface. Interestingly, they exhibit superior bubble absorption capabilities in an underwater situation which is complementary to a droplet impinging on the same surface in an air medium. In the present work, we examine closely, an experimental paradigm describing the physical aspects of such an absorption event and delineate the nature of evolution of the most important parameter, the contact line. The results provide insight into the efficient development of underwater bubble absorbers for hydrocarbon industry for a safe transfer of gases from deep sea oil rigs.

1. Introduction
Superhydrophobic surfaces which are extreme repellants of water have gained much attention in the recent past due to their applications in the area of self-cleaning [1,2], anti-icing [3,4], thermal management [5,6] and microfluidics [7,8] to name a few. They are characterized by low surface energy that can repel any water droplet that interacts with it, thus the name ‘superhydrophobic’. Typically, a water contact angle (commonly used method to characterize the wetting of a surface) value of more than 90° is termed as hydrophobic and those with less than 90° is called ‘hydrophilic’. However, for extreme contact angles, typically more than 150° are called ‘superhydrophobic’. Interestingly, it is not only the surface material properties that dictate the contact angle, but also the structural features on the surface which creates a particular roughness profile on the surface. A rough surface can aid in the formation of air pockets when a droplet is placed over it and thus providing a cushioning effect. This will facilitate an easy detachment of the droplet and thus it can roll off easily. In nature, it is seen in the lotus leaves, as an evolutionary adaptation of the aquatic plants to repel water droplets on it to survive during splashing and heavy rain and thus sometimes is also referred to as the ‘lotus leaf effect’. Recently, several researches have aimed at biomimetically engineering such structures on surfaces like polymers to create the same effect of this repellency [9,10]. In terms of the wetting configuration, they are classified as the Cassie-Baxter state of wetting where the structure induced cushioning results in the roll-off opposed to the Wenzel state where the roughness elements are invaded by the water droplet and not showing a roll-off and is rather pinned to the surface [11]. These are quantified through the dynamic contact angle measurement where an advancing contact angle measurement while the contact line just start moving out of the droplet and invades fresh and
unwetted surface) and receding contact angle (angle measured while the contact line just start to retract back to an already wet surface) are estimated and their difference yields the contact angle hysteresis. In brief, a surface with high contact angle hysteresis corresponds to a more wetting surface where the roll-off is minimal whereas the opposite will give a high roll-off and thus easy detachment of the droplet. In a dynamic situation like the impact, the superhydrophobic surfaces show remarkable bouncing and elastic behavior, entirely different from that of a hydrophilic surface where spreading is observed.

During underwater exploration of the hydrocarbons from deep sea, it is necessary to have specialized gas collection mechanisms for faster removal and to mitigate dangers of explosion. In this regard, porous membranes are helpful in absorbing the bubbles over a large area. For such a scenario, a porous superhydrophobic membrane can serve as an excellent candidate for the bubble absorption. It is a complementary configuration of a droplet falling on a solid surface in air medium where the role of gravity on the droplet is played by the buoyancy on a rising bubble. There are a few works focused on the concept of terminating the bubbles using superhydrophobic sponges[12,13], but a detailed study including the observable wetting parameters were not to be found in the literature. In this work, we carefully experiment such a system in its simplest terms and extract the most important parameter: the contact line and its evolution with time. The physical reasoning behind the temporal variation of the contact line is explained form the fundamental principles of force balance.

2. Materials and methods

2.1. Experimental setup

We used a Polytetrafluoroethylene (PTFE) based porous membrane of thickness \(b\) (Porex, USA) housed within a Poly(methyl methacrylate) (PMMA) cavity as the bubble absorber. A perforated PMMA sheet was used as the back support for the membrane as shown in Figure 1. The entire cavity is housed inside a water tank which is fixed using a chemical stand and can vary the angle at which it is placed with respect to the horizontal axis \((\alpha)\) and at a height \(H\) as shown in Figure 1. At the bottom of the tank, a custom-bubble dispenser made from surgical needle and luer-lock is placed and air is slowly pumped at a flow rate of \(Q\) into it externally from a syringe pump. This results in the dispensation of air bubbles from the dispenser with a diameter \(d \approx 1.75\) mm at a velocity of \(u \approx 0.3\) m/s. This droplet is then impacted on the membrane and starts to spread with a contact line length of \(L\) and an air contact angle \(\theta\) which are a function of time. Quickly, the bubble is absorbed into the membrane and disappears. A tubing connects the cavity to the atmosphere through the water and thus facilitates the expulsion of air absorbed as bubbles, to the outside air at the atmospheric pressure \(p_{\text{atm}}\). A high-speed camera (Photron FASTCAM SA6) at a resolution of 1024 \(\times\) 1024 square pixels is used to capture the bubble impact and subsequent events of spreading and absorption at 5000 frame per second. Later, the images are analyzed using an in-house developed code in MATLAB.

![Figure 1](image_url)  
**Figure 1.** (a) Experimental setup showing the bubble absorption mechanism. The cavity is immersed inside a water filled tank at an angle \(\alpha\) and at a depth \(H\) below the reference of the free water surface. A custom-made bubble dispenser release air bubbles with diameter \(d\), which due to buoyancy, ascents at a velocity \(u\) and impacts on the membrane and spreads with a time varying contact angle \(\theta\) and contact line \(L\). (b) Photograph of a bubble about to impact the membrane. Scalebar 1mm.
2.2. Surface characterization

As the material should be characterized for its structural and topological aspects, we have carried out the scanning electron microscopy (SEM) as shown in Figure 2. At a 500x magnification, the micro/nano features are visible on the surface, which are responsible for the structural superhydrophobicity offered by the Cassie-Baxter wetting state. Further, the roughness profile is estimated from the atomic force microscopy (AFM) as shown in Figure 3 and the average roughness value ($R_a$) was found to be 4.5 μm.

![Figure 2](image1.png)

**Figure 2.** Scanning Electron Microscopic image showing the hierarchical micro/nano features that are responsible for the superhydrophobic nature of the surface.

![Figure 3](image2.png)

**Figure 3.** Atomic force microscopic profile to estimate the topology and the average roughness of the membrane surface.

3. Results and discussion

The contact line evolution with respect to time is plotted in Figure 4 with error bars representing the standard deviation from four sets of experiments. Upon contact with the surface, $L$ is quickly increased as the bubble spreads and reach a maximum point. At the same time, the absorption takes place and the bubble is eventually absorbed into the membrane completely with the gas (air) transported through the tubes and eventually expelled to the atmosphere. As contact line is the most important parameter along with the contact angle in any wetting scenario, the time evolution of the contact line can give a clue about the parameters like absorption time and the droplet geometry. It is not so obvious to gain any physical insight from the Figure 4 and thus the same is plotted in log scale in Figure 5 from which we can extract the slope of the temporal evolution easily by fitting a linear curve.
Figure 4. The contact line (L) evolution of the bubble with time.

From Figure 4, we obtain a slope of ½ in the initial regime of spreading from the fitted line. This can be explained from the balance of hydrostatic pressure: $\rho g H$ and dynamic pressure: $\rho \left(\frac{dL}{dt}\right)^2$ as the gravitational effect surpasses the surface tension effect. Here, $\rho$ is the density of water and $g$ is the acceleration due to gravity and $V$ is the volume of the bubble. Comparing the two pressures, $\rho g H \sim \rho \left(\frac{dL}{dt}\right)^2$, we can estimate the scaling for $L$ as: $L \sim (gV)^{\frac{1}{4}} t^{\frac{1}{2}}$. This elucidates the source the scaling relationship as observed from the experiment. However, one of the serious implications for this scaling here is in the prefactor $(gV)^{\frac{1}{4}}$ that the volume of the bubble should stay constant for the period. Although it stays constant for some period when the penetration has not started significantly, this is obeyed whereas towards reaching the maximum point, we can observe the deviation from the curve. After the peak, the sudden decrease is exponential, implying a quick removal of the bubble from the surface.

Figure 5. The log plot of Figure 4 showing the linear scale with the slope of ½ in the initial regime of spreading (marked red) signified by the physical forces in action.

The absorption time ($\tau$) is plotted with respect to the impact angle in Figure 6. This is the time taken by the bubble to get completely absorbed into the membrane from the first instance of touching. It is found that with an increase in the impact angle, $\tau$ is increased almost linearly within the range of 0-60°. Beyond this, the bubbles may evade the membrane and will just slide off, without any attachment points. As the bubble approaches the membrane, it squeezes the water film that is between the bubble and the membrane and thus get deformed by itself in the process. This elongates the bubble
and thus have a larger area of contact while it touches. Also, there is a time delay from the first instant of touching of the droplet and a complete flattening on an inclined membrane compared to a flat membrane. This can increase the absorption times significantly as the angle increases.

**Figure 6.** The variation of absorption time $\tau$ with respect to the impact angle $\alpha$.

4. **Conclusion**
The present work investigates the physics behind the interaction of a bubble with a porous membrane. With an aim to provide fundamental insights into the physical mechanisms behind the bubble impact, spreading and the subsequent absorption into the membrane. It is a starting point for future works to study the deeper aspects of bubble absorption in underwater medium and innovate safer designs for the absorption of hydrocarbons in oil and natural gas industry, to reduce the fatalities in offshore oil rigs.

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